A TEXTBOOK OF PRACTICAL PHYSICAL CHEMISTRY

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BY

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WITH A PREFACE BY

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AUTHORS' PREFACE TO ENGLISH EDITION

AS explained in the preface (written in February, 1929) to the German edition, this addition to the number of already existing books on practical physical chemistry had as its starting-point a course of instruction which was in use in the chemical laboratory of the University of Munich, and in the Universities of Erlangen and Würzburg; this course itself originated in the Institute of Professor G. Bredig at the Technische Hochschule in Karlsruhe, and was modified as time went on.

The object of the book being to make it possible for the practical work to be carried out with a maximum of self-reliance on the part of the student and with a minimum of assistance from instructors, the experimental instructions have been given in great detail; and in order that the laboratory work may provide as much profit on the theoretical side as possible, full attention has been devoted to the theory of each experiment. The explanations of theory are not intended to take the place of textbooks, but merely to draw the attention of the student to all the points which he must of necessity grasp clearly in order to work through the experimental problem with full understanding and profit; usually a fuller explanation of these points should be sought in the textbooks. Special attention has been devoted to points, both theoretical and practical, which experience has shown are repeatedly raised by students.

The authors feel that it is perhaps a deficiency in the theoretical explanation that the modern point of view about strong electrolytes is not given sufficient prominence, especially

in the section on electromotive forces, which are discussed in terms of concentrations instead of activities; but they consider that to introduce the new system into this book would involve too great a departure from the treatment at present given in most of the general textbooks.

The authors wish to express their thanks to Professor G. Scheibe for providing the material of sections II, XIII and XIV, and to Dr. H. Kroepelin for the material of sections III and IV; to Professor K. F. Herzfeld, with whom the whole plan of the book was discussed; to Professors G. Bredig, H. G. Grimm, and G. Scheibe for their friendly advice and criticism of the manuscript; to Dr. E. Lange, Dr. G. Wagner, Dr. H. Fromherz, and Dr. P. Wulff for suggesting numerous improvements.

Since the publication of this book it has come into use in some other German universities in addition to those mentioned above. A Russian translation is in the Press, and a Spanish is in course of preparation. In the present English edition a few points have been modified which applied only to the universities for which the book was originally intended, and a few improvements have been included based upon experience obtained since the publication of the book.

The authors wish to express their thanks to Mr. B. Topley for the care which he has bestowed upon this translation, which faithfully reproduces the original.

K. FAJANS
J. WÜST

MUNICH
July, 1930

PREFACE

IT gives me very great pleasure to write a brief introduction to this excellent work on Practical Physical Chemistry by Fajans and Wüst. Not only is Professor Fajans known to the scientific world as one of the most distinguished investigators in the field of Physical Chemistry, but he has also had much and varied experience in the training of University students.

This book covers a very wide field and is characterised by many highly commendable features. In the case of every measurement the relevant theory is clearly indicated, and detailed references are given to those parts of well-known works where the student can obtain full information concerning the theoretical basis. Every teacher of Physical Chemistry will welcome this feature of the book, as it not only lightens his labour but also assists greatly in keeping theory and experiment together in the mind of the student.

The authors have also earned our gratitude by including in the scope of their work such important matters as radioactive transformations, spectrophotometric measurements, ultra-violet spectrography, metallography, potentiometric titration, the quinhydrone electrode, etc.

The descriptions of the experimental work are clear and explicit, but not such as to endanger the student's development of practical sense and manipulative skill.

The book has been admirably translated by Mr. Bryan Topley, and will be used in the Chemical Laboratory of University College.

F. G. DONNAN

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PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE,
LONDON, *October, 1930.*]

CONTENTS

THE following books are referred to frequently, and are cited under the authors' names :—

Eucken, Jette, and Lamer. Fundamentals of Physical Chemistry. 1925.

Nernst. Theoretical Chemistry. English Edition, revised in accordance with the 8th-10th German editions. 1923.

Reilly, Rae, and Wheeler. Physico-Chemical Methods. 1926.

A Treatise on Physical Chemistry. Edited by H. S. Taylor.

Ostwald-Luther. Hand-und Hilfsbuch zur Ausführung Physico-chemische Messungen. 4th edition. 1925.

References to text-books and monographs other than these, and to journals, are given in full in the text.

PRACTICAL PHYSICAL CHEMISTRY

GENERAL INTRODUCTION

(a) Recording Observations and Calculations

ALL observations and measurements and diagrams of connexions and of special arrangements of apparatus should be accurately and clearly entered in a special note-book—not simply recorded on loose sheets. The records should be so complete that later, even after an interval of years, the course of the experiment can be quite clearly reviewed. It is important to trust nothing to memory. The record in the book should be such that a person unacquainted with the work could make the calculation of the result of the experiment. The recorded observations and the corresponding numerical calculations made to obtain the result should be kept quite separate; they may be arranged either in sequence or upon opposite sides—e.g. observations on the left, calculation on the right. It is desirable that all the working should be kept in the note-book, and not on loose sheets.

(b) Accuracy and Reproducibility

Usually, the final result is obtained as the result of making a series of individual measurements. Thus, to determine a molecular weight by the freezing-point method weighings of the solvent and of the solute and readings of the thermometer are required. The relationship between the individual measurements and the final result thus depends upon the particular case. The quantity required may, for example, be the sum or the difference of various measured quantities, or it may be directly or inversely proportional to them. There may also be proportionality to some function of a measured quantity, such as a power or a root, or the logarithm or sine. Accordingly, the effect of an error in an individual measurement upon the final result also depends upon the special circumstances. For the

sake of saving labour one must consider, before beginning the experiment, with the aid of known relationships such as have been mentioned, what accuracy is required in the individual measurements, and hence how sensitive need be the methods of measurement selected, in order to obtain a specified accuracy in the final result. If the accuracy of the individual measurements is not the same, then the error in the final result is mainly determined by the error in the quantities which are least susceptible of accurate measurement. If the accuracy with which the other quantities may be determined is five to ten times that of the least exactly measurable quantity, then the influence of error in the former upon the final result may be neglected. A few examples will make clear how these considerations should be applied:

(1) In a molecular weight determination by the boiling-point method the molecular weight m is related to the weight of dissolved substance g, the weight of the solvent G and the rise of boiling-point ΔT by the formula $m = K \cdot \frac{g \cdot 1000}{G \cdot \Delta T}$. K is the "boiling-point constant" which is assumed to be known exactly. Since in this case m is either directly or inversely proportional to each of the quantities to be determined, a definite percentage error in any one of these quantities causes an equal percentage error in the final result. (Thus if one measures $g = 0{\cdot}3$ gm. *ca.* with an accuracy of only 1 per cent. $= \pm 0{\cdot}003$ gm. then the uncertainty in m is also 1 per cent., i.e. when $m = 150$, it equals $\pm 1{\cdot}5$.) In the present case the quantity least susceptible of precise measurement is ΔT. In general ΔT is of the order $0{\cdot}2°$ to $0{\cdot}4°$. Using a Beckmann thermometer, at the best the temperature can be read to a thousandth part of a degree, with the aid of a lens. But in any case the mercury thread does not set itself more exactly than to about $^1/_{1000}°$, depending among other things upon the vigour with which it is tapped. The accuracy of the individual temperature readings is therefore not greater than about $^2/_{1000}°$. Measurement of the temperature difference involves two readings; the difference may therefore be affected by an error of up to $^4/_{1000}°$ (= 1 to 2 per cent. in $0{\cdot}4$ to $0{\cdot}2°$). Thus m cannot be determined with an accuracy greater than 1 to 2 per cent. even when, as is not difficult, g and G are measured to within $0{\cdot}1$ per cent.; with these quantities, therefore, an accuracy of from $0{\cdot}1$ to $0{\cdot}2$ per cent. is quite sufficient. Hence the substance (*ca.* $0{\cdot}3$ gm.) should be weighed on an analytical balance accurately to $0{\cdot}1$ or $0{\cdot}2$ mg., while for the determination of G (*ca.* 30 gm.) a rougher balance is used,

with which the weight may be determined to the nearest ·01 gm. (cf. pp. 22 and 28).

(2) The correction for the buoyancy of air when weighing with brass weights amounts to 0·15 per cent. for a substance of specific gravity $s = 0{\cdot}7$, to 0·1 per cent. for $s = 1$, and to 0·05 per cent. for $s = 1{\cdot}9$. If the accuracy of the remainder of the measurement is of this order, then neglect of the correction for buoyancy causes an error in the result of the measurement which cannot be ignored.

(3) Equal *absolute* temperature changes produce equal *relative* changes of the electrical conductivity of electrolytes. A rise in temperature of 1° usually corresponds to an increase in conductivity of from 2 to 3 per cent. Therefore, if agreement to within 0·2 per cent. is to be obtained among the individual values when the same measurement is repeated, the temperature must be kept constant to within 0·1° or 0·07°. (Cf. p. 151.)

(4) In kinetic measurements a rise of temperature of about 10° doubles or trebles the reaction velocity, so that a rise in temperature of $n \,.\, 10°$ causes a 2^n- or 3^n- fold increase in velocity. The following calculation shows that in a series of measurements the velocity constants will agree among themselves to within 1 per cent. only if the fluctuations in temperature do not exceed 0·14° or 0·09°. (Cf. p. 104.)

$$1{\cdot}01 = 2^n\,;\ \log 1{\cdot}01 = n \,.\, \log 2\,;\ n = \frac{\log 1{\cdot}01}{\log 2} = \frac{0{\cdot}00432}{0{\cdot}3010}$$
$$= 0{\cdot}014\,;\ 0{\cdot}014 \times 10° = 0{\cdot}14°.$$

(5) In conductivity measurements the unknown resistance w_x is found by multiplying the known resistance w by $\frac{a}{1000 - a}$, where a is the position on the bridge wire (expressed in mm.) of the sliding contact when the minimum of sound is obtained. The sensitivity of the telephone used is such that the position of minimum sound may be found to within 1 mm., i.e. to $\pm \frac{1}{2}$ mm. But as the formula shows, an error of 1 mm. in the setting affects w_x differently at different positions on the bridge; thus at the setting 100 mm. or 900 mm. an error of 1·1 per cent. is produced (100 : 900 = 0·1111; 101 : 899 = 0·1123); at 200 mm. or 800 mm. the error amounts to 0·6 per cent. (200 : 800 = 0·2500; 201 : 799 = 0·2516); while at the middle of the bridge, with a setting of 500 mm., the error is only 0·4 per cent. (501 : 499 = 1·0040). With the same absolute sensitivity, the greatest accuracy is obtained by so arranging matters that the point of

balance falls as nearly as possible in the middle; and in any case it should be between 300 and 700 mm. (Cf. p. 161.)

(6) The sensitivity of the capillary electrometer used in the measurement of E.M.F. is about $\frac{1}{2}$ millivolt. In order to calculate how accurately the concentrations of the solutions employed must be defined so that the error arising from this source may have practically no influence upon the E.M.F., use is made of the fact that the electrode potential in the case of uni-univalent electrolytes is given by the expression $\epsilon_h + 0{\cdot}058 \log_{10} c$ volts. ϵ_h is the normal potential and hence a constant independent of c. (Cf. p. 181.) An alteration of the quantity (58 log c millivolts) by $\frac{1}{2}$ millivolt corresponds to an alteration in log c of about 1 per cent., that is, to an alteration of the log from 1·00 to 1·01. From the logarithm table it is found that this corresponds to an alteration in c of about 2 per cent. An error of 0·2 per cent. in the concentrations assumed for the solutions is therefore without appreciable influence upon the accuracy of the results obtainable by this method; consequently in preparing the solutions to be used it is sufficient to weigh both the water and the salts with an accuracy of about 0·1 per cent.

(c) Averaging; mean deviation from the mean; mean error of a single determination and of the mean; probable error

It is usual, in arriving at the final result and also in measuring the intermediate quantities, to make several determinations. The separate values obtained almost always differ more or less, the differences arising from the *accidental* errors of observation and measurement which influence the results of the various measurements more or less strongly, sometimes in one direction and sometimes in the other, and which, with a very large number of observations nearly neutralise one another in the average. The simplest procedure to obtain the *most probable value* is to take the *arithmetical mean*:

$$R_m = \frac{R_1 + R_2 + R_3 + \ldots R_n}{n}.$$

The calculation of the mean is much simplified by using only the decimal places in which the individual values differ. The procedure is to start with some round number lying approximately in the middle, as a starting-point, and find the differences of the separate values from this provisional mean. The + and − differences are then separately added up and the difference of the sums is divided by n. The figure obtained is (according to

its sign) added to or subtracted from the provisional mean. For example, to find the mean value of 0·01325; 0·01329; 0·01321; 0·01317; 0·01333; 0·01319, the provisional mean is taken as 0·01320; the separate differences in the fifth decimal place are then $+5+9+1+13-3-4=+24$, divided by $6=+4$. The true mean is therefore 0·01324.

In taking the mean, *all* observations are to be included. Only when there has previously been reason to suspect a particular measurement of being faulty (a fact which should evidently be recorded during the experiment in question) should the result of this measurement be omitted in taking the mean; a case in point would be when one believes that the weights have been interchanged, or that a thermometer has been misread, or when during a kinetic or a conductivity measurement the temperature had been very inconstant. Furthermore, personal fatigue towards the end of a long or very trying series of measurements is prejudicial to the attentiveness of the observer and therefore to the accuracy of the readings. This should be taken into account by attributing less value to measurements obtained towards the end. In such cases the measurement in question is not always simply rejected entirely, but instead, in taking the mean a smaller "weight" is allowed to it, in the following way: the measurements which are not in doubt are given the weight 1, and to those to which there is some objection are allotted the weights $\frac{1}{2}$ or $\frac{1}{4}$ according to circumstances. The mean is found by adding up the modified individual values and dividing by the sum of the individual weights:

$$R_m = \frac{R_1 \cdot 1 \cdot + R_2 \cdot 1 + R_3 \cdot \frac{1}{4} + R_4 \cdot \frac{1}{2} + R_5 \cdot 1 + R_6 \cdot \frac{1}{4}}{4}.$$

Naturally the subjective element comes into play to some extent in allotting the individual weights; but the precise reason for regarding a result as of lesser importance should be stated at the time in the note-book. *The reason for attaching less weight to a particular value ought never to be merely the fact that it deviates more widely from the mean value than all the others.* It is always possible that for once the fortuitous errors have all been in the same direction.

As a measure of the magnitude of the individual deviations, and therefore also for the "reproducibility" of a result either the "mean deviation from the mean" or the "mean error of a single determination" or the "mean error of the mean" may be taken. The mean deviation from the mean is evaluated by taking the arithmetical mean of the separate errors (= de-

viations of the separate measurements from the mean) without reference to their signs. In the example above it was

$$10^{-5} \cdot \frac{1+5+3+7+9+5}{6} = 5 \cdot 10^{-5} = \pm 0{\cdot}00005.$$

The mean error of an individual measurement (m.e.) is given by the formula

$$\text{m.e.} = \pm \sqrt{\frac{\Sigma\Delta^2}{n-1}} \quad . \quad . \quad . \quad (1)$$

Δ is the deviation of each measurement from the mean, n the number of measurements. The formula is only valid in this simple form when all the results to be combined into a mean are of equal weight. In the above example $\Delta_1 = +1$; $\Delta_2 = +5$; $\Delta_3 = -3$; $\Delta_4 = -7$; $\Delta_5 = +9$; $\Delta_6 = -5$;

$$\Sigma\Delta^2 = 1 + 25 + 9 + 49 + 81 + 25 = 190;$$

$$\text{m.e.} = \pm 10^{-5}\sqrt{\frac{190}{5}} = \pm 0{\cdot}000062.$$

For calculating the mean error of the mean (M.E.) the formula used is

$$\text{M.E.} = \pm \sqrt{\frac{\Sigma\Delta^2}{n(n-1)}} \quad . \quad . \quad . \quad (2)$$

In the present case the M.E. amounts to $\pm 10^{-5}\sqrt{\frac{190}{6 \cdot 5}} = \pm 0{\cdot}000025$. It can be seen from these formulæ that although the mean deviations and the mean errors of the individual determinations are not decreased by increasing the number of determinations, still these errors become more exactly defined in respect of magnitude. On the other hand, the mean error of the mean is smaller, the larger the number of measurements. Frequently the "probable error" of an individual determination or of the mean is also given. This is found by multiplying the m.e. or the M.E. by 0·6745, that is by about $\frac{2}{3}$. This gives a number of which it can be said that the actual error is as likely to be greater as to be smaller.

All these calculations refer only to the distribution of individual results about a mean value in so far as they are dependent upon *accidental errors*. These influence the *reproducibility* or the *relative accuracy*. A sharp distinction must be made between these, and the "systematic errors" upon which depends the *correctness* or the *absolute accuracy* of a result. The latter arise from imperfections in the method of measurement, either faulti-

ness of the apparatus used, or neglect of some important correction, or, evidently, through limitations of the observer himself (e.g. tardy recognition of the change of an indicator owing to insensitivity of the eye to colour). They can also be caused by insufficient purity of the materials used. Such systematic errors affect all the individual measurements and therefore also the final result in the same sense. Therefore, they do not tend to compensate mutually on making many experiments and taking the mean of the individual results, but they do not influence the reproducibility of a measurement. The *correctness* of the value found depends upon their recognition and elimination. They are only to be avoided, first by careful purification of all substances used, and accurate testing and calibration of the measuring instruments used (burettes, pipettes, measuring flasks, thermometers, resistances, bridge wires, normal cells, etc.), and second by a control of the investigation by the aid of another method, different apparatus and different observers.

The numerical magnitude of each individual quantity should be given to as many places as is consistent with the last but one being certain, and the last uncertain to less than five units. This applies both to the separate readings of different instruments and to the results calculated from these readings. If a thermometer graduated in whole degrees is read as exactly 14°, 14·0° should be recorded since the tenths can be estimated; but with a thermometer graduated in hundredths, 14·000 should be written, since then only the thousandths are uncertain. For the calculation it is advisable to use one decimal place more than is finally required. Thus in a molecular weight determination one may calculate individual values such as 117·8; 119·2; 116·4; but the large mean error shows at once that the last place has no significance, and in the final statement of the result it should be omitted. If the approximate accuracy of the method is known at the outset, then it is possible to avoid carrying an unnecessary number of decimal places through the calculation. In the practical exercises described in this book a four-figure logarithm table is almost always sufficient, five figures being required only in the calculation of molecular refraction. The accuracy of a good slide rule (0·1 to 0·2 per cent.) is often sufficient, particularly for approximate calculations. In physical chemical calculations it is advisable to form the habit of thinking and calculating in gram mols. and gram equivalents. Many calculations are remarkably simplified thereby.

References :—
Ostwald-Luther. Chap. I.
Reilly, Rae, and Wheeler. Chap. I.

I. MOLECULAR WEIGHT DETERMINATIONS IN SOLUTIONS

(a) Theory

(1) THE osmotic pressure produced by the dissolved molecules in a solution is equal to the gas pressure which the same molecules would exert if they were in the gaseous state and occupied the same volume at the same temperature as in the solution. Hence according to van't Hoff the gas equation may be applied to the osmotic pressure:

$$p_{\text{osm.}} \cdot v = n \cdot \mathrm{R} \cdot \mathrm{T}$$

n is the number of dissolved mols, R the gas constant $= 0{\cdot}082$ Lit. Atm./1° if p is measured in atmospheres and the volume v of the solution in litres; T is the absolute temperature. Putting $\frac{n}{v} = c$ (Mol./Lit.) then

$$p_{\text{osm.}} = c \cdot \mathrm{R} \cdot \mathrm{T}.$$

Accordingly the measurement of osmotic pressure can be applied to the determination of the molecular weights of dissolved substances, just as the molecular weight of a gaseous substance is found by measurement of the vapour pressure and vapour density. But owing to the difficulties and the long duration of the experiment, this method is unsuited to ordinary work in the laboratory. It is more convenient to start from the fact that solutions of equal osmotic pressure, i.e. solutions of equal molar concentration, show the same lowering of vapour pressure with respect to the pure solvent. The connexion between the magnitude of the vapour pressure lowering and the concentration of the solution is given by Raoult's law, which was originally discovered empirically, but may be deduced kinetically:

$$\frac{p_0 - p}{p_0} = \frac{n}{n + \mathrm{N}}.$$

p_0 is the vapour pressure of the pure solvent, p the partial pressure of the solvent over the solution. The conditions for the applicability of the method are that the dissolved substance does

not react with the solvent and is not volatile, and under these conditions p is the vapour pressure of the solution. n is the number of mols of dissolved substance, N the number of mols of solvent in the solution. For very dilute solutions n may be neglected in the denominator in comparison with N, and the law then takes the simple form

$$\frac{p_0 - p}{p_0} = \frac{n}{N} \quad . \quad . \quad . \quad . \quad (3)$$

Since accurate vapour pressure measurements are also inconvenient to carry out, the rise in boiling-point or the lowering of the freezing-point of the solution with respect to the solvent is determined; these are proportional to the lowering of the vapour pressure. The connexion between lowering of vapour pressure and rise in boiling-point may be seen by reference to Fig. 1.

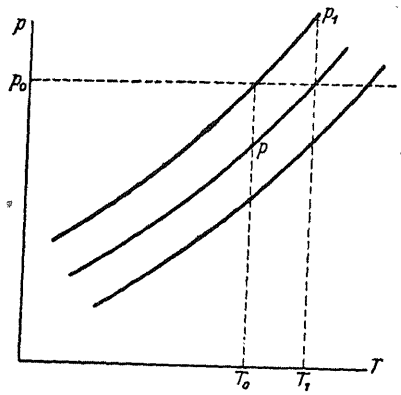

FIG. 1.

In the vapour pressure temperature diagram, the upper curve shows the increase of vapour pressure with temperature of the pure solvent, and the two lower curves refer to solutions of two different concentrations. The curves do not run exactly parallel; nevertheless they may be taken as parallel over short corresponding stretches, without large error. This is important for the following considerations, which apply only to dilute solutions.

(2) In the boiling-point method the temperatures are measured, at which the pure solvent (T_0) and the solution (T_1) boil—i.e. have a vapour pressure equal to the external (atmospheric) pressure (p_0). (*Boiling* is characterised by bubbles of vapour rising *from the interior of* the liquid; it differs in this respect from *evaporation* which at every temperature takes place at a rate depending, among other factors, upon the vapour pressure, but from the *surface* only, through molecules diffusing from the surface into the space outside.)

The temperature difference between the two boiling-points T_1 and T_0 is related to the vapour pressure lowering $p_0 - p$ as follows: since the two curves are approximately parallel the

increase of vapour pressure of the solution $(p_0 - p)$ in the temperature interval $T_1 - T_0$ may be taken as equal to the increase of vapour pressure of the pure solvent $(p_1 - p_0)$ in the same temperature interval. In this small interval the vapour pressure curve is assumed to be linear, and therefore

$$\frac{dp}{dT} = \frac{\Delta p}{\Delta T} = \frac{p_1 - p_0}{T_1 - T_0}, \text{ so that } p_1 - p_0 = (T_1 - T_0)\frac{dp}{dT}.$$

Since according to the Clausius-Clapeyron equation

$$\frac{d \log_e p}{dT} = \frac{dp}{p \,.\, dT} = \frac{\Lambda}{RT^2},$$

where Λ is the molar heat of condensation, it follows that

$$\frac{p_1 - p_0}{p_0} = (T_1 - T_0)\frac{\Lambda}{RT^2}.$$

Further, because of the parallelism of the two curves,

$$\frac{p_1 - p_0}{p_0} = \frac{p_0 - p}{p_0},$$

and this, according to Raoult's law $= \frac{n}{N} = \frac{g \,.\, M}{m \,.\, G}$, where g and m are respectively the weight and the molecular weight of the dissolved substance, and G and M the weight and molecular weight of the solvent. Hence

$$T_1 - T_0 = \frac{g \,.\, M \,.\, R \,.\, T^2}{m \,.\, G \,.\, \Lambda}.$$

The expression $\frac{M \,.\, RT^2}{\Lambda} = \frac{RT^2}{\frac{\Lambda}{M}} = \frac{RT^2}{\lambda}$, in which λ represents the specific heat of condensation (= heat of condensation per 1 gm.) has a definite constant value for every solvent. It is usual, however, to choose as the *constant of boiling-point raising* (the ebullioscopic constant or the molecular boiling-point raising) a value 1000 times smaller, and accordingly to multiply the expression $\frac{g}{m \,.\, G}$ by 1000. Then

$$T_1 - T_0 = K \,.\, \frac{g \,.\, 1000}{m \,.\, G}, \text{ where } K = \frac{RT^2}{\lambda \,.\, 1000} \qquad (4)$$

The constant K gives, therefore, the rise in boiling-point which results when 1 mol $\left(\frac{g}{m} = 1\right)$ is dissolved in 1000 gms. of solvent ($G = 1000$). From the observed raising of the boiling-point the molecular weight is found by means of the formula

$$m = K \cdot \frac{g \cdot 1000}{G \cdot (T_1 - T_0)} \quad . \quad . \quad . \quad (5)$$

The value of K for ether is 2·10, for benzene 2·70, and for water 0·519.

(3) In the cryoscopic method the lowering of the freezing-point of solution with respect to pure solvent is measured. This is proportional to the vapour pressure lowering; the connexion between the two quantities may be deduced by reference to Fig. 2, which represents the vapour pressure temperature diagram of a solvent and two solutions of different concentration in the neighbourhood of the freezing-point. CA is the vapour pressure curve of the solid, AB that of the liquid solvent. At the point A, where the solid and the liquid have the same vapour pressure, the two phases are in equilibrium. A is the melting- or freezing-point, and the corresponding temperature T_0 is the melting or freezing temperature. A′B′ and A″B″ are the vapour pressure curves of two solutions of different concentrations. Because of the lowering of vapour pressure these cut the curve AC at temperatures lower than T_0. Making the important assumption that the pure solvent separates from the solutions, and not either mixed crystals or a eutectic mixture, then this separation of solid solvent first occurs at a lower temperature than with the pure solvent. The lowering of freezing-point may be calculated from the vapour pressure lowering as follows:

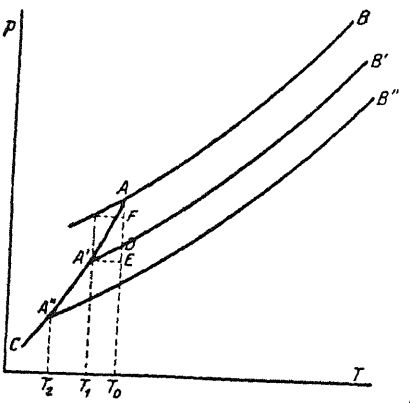

FIG. 2.

From Fig. 2 it can be seen that the vapour pressure lowering AD of one of the solutions is equal to the difference between

the decrease of vapour pressure of the solid phase in the temperature interval $T_0 - T_1$ (= AE) and the decrease of vapour pressure of the solution in the same interval (= DE). Taking these two curves as linear over small distances, then

$$AE = (T_0 - T_1) \cdot \frac{dp_{\text{solid}}}{dT}; \quad DE = (T_0 - T_1) \cdot \frac{dp_{\text{solution}}}{dT}.$$

Further assuming that the vapour pressure curve of the solution is parallel to that of the pure liquid solvent, then instead of DE the decrease AF of the vapour pressure of the pure solvent between T_0 and T_1 may be introduced:

$$DE = (T_0 - T_1) \cdot \frac{dp_{\text{solvent}}}{dT}.$$

But according to the Clausius-Clapeyron equation

$$\frac{dp_{\text{solid}}}{dT} = \frac{\Lambda_s p_0}{RT^2},$$

where Λ_l is the molar heat of condensation of the solid solvent, while

$$\frac{dp_l}{dT} = \frac{\Lambda_l p_0}{RT^2},$$

where Λ_l is the molar heat of condensation of the liquid solvent. Hence

$$AD = p_0 - p_1 = AE - DE = (T_0 - T_1)\frac{dp_s}{dT} - (T_0 - T_1)\frac{dp_l}{dT}$$

$$= (T_0 - T_1)\frac{\Lambda_s p_0}{RT^2} - (T_0 - T_1)\frac{\Lambda_l p_0}{RT^2}$$

$$= (T_0 - T_1)\frac{p_0}{RT^2}(\Lambda_s - \Lambda_l).$$

But $\Lambda_s - \Lambda_l$ is equal to the heat of crystallisation $\Lambda_{cr.}$, so that the formula runs

$$\frac{p_0 - p_1}{p_0} = \frac{\Lambda_{cr.}(T_0 - T_1)}{RT^2}.$$

By Raoult's law

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N} = \frac{g \cdot M}{m \cdot G}$$

so that

$$T_0 - T_1 = \frac{g \cdot M \cdot RT^2}{m \cdot g \cdot \Lambda_{cr.}} = \frac{g \cdot RT^2}{m \cdot G \cdot \lambda_{cr.}}$$

where $\lambda_{cr.}$ is the specific heat of crystallisation (heat of crystallisation of 1 gm.).

The expression $\frac{RT^2}{\lambda_{cr.}}$ is another constant characteristic of the particular solvent; but here also, just as with the boiling-point raising, the *freezing-point lowering constant* (cryoscopic constant or molecular lowering of the freezing-point) is chosen so that it is 1000 times smaller: $K = \frac{RT^2}{\lambda_{cr.} \cdot 1000}$. Then

$$T_0 - T_1 = \frac{g \cdot 1000}{m \cdot G}\left[\frac{RT^2}{\lambda_{cr.} \cdot 1000}\right] = K \cdot \frac{g \cdot 1000}{m \cdot G} \quad . \quad (6)$$

The cryoscopic constant gives the lowering of freezing-point which results when 1 mol. of a substance is dissolved in 1000 gms. of solvent. For benzene it is 5·13 and for water 1·860. From the observed lowering of the freezing-point the required molecular weight of the dissolved substance is found from the formula

$$m = K \cdot \frac{g \cdot 1000}{G(T_0 - T_1)} \quad . \quad . \quad . \quad (7)$$

Note.—The expression for the molar lowering of the freezing-point can also be deduced in the following way, which is based directly upon the second law of thermodynamics: let T_0 be the freezing-point of the pure solvent, T_1 the (only very slightly different) freezing-point of a very dilute solution of concentration n mols in 1000 gms. of solvent. A cyclic process is performed, starting with a large quantity of the solution which at temperature T_1 is in equilibrium with $\frac{1000}{n}$ gm. of solid solvent, i.e. the quantity which in the solution is associated with 1 mol of dissolved substance. (1) The solution and the solid phase are separated and warmed to T_0. (2*a*) At T_0 the solid solvent is melted, with absorption of the heat of fusion $Q = \frac{1000}{n} \cdot \lambda_f$ (λ_f is the specific heat of fusion = heat of fusion per 1 gm.). (2*b*) The quantity of pure liquid solvent so obtained is reversibly added at T_0 to the main quantity of solution, by means of a semi-permeable membrane. Thereby the osmotic work $p \cdot v = R \cdot T_0$ is obtained, where p is the osmotic pressure of the solution, v the volume of $\frac{1000}{n}$ gm. of solvent, in which just 1 mol of the solute is contained. (3) The whole solution is cooled again to T_1, whereby, apart from small quantities of the second order, the quantity

of heat previously used in warming the system is obtained back again. (4) In the last step, $\frac{1000}{n}$ gm. of solvent are allowed to freeze out at T_1, whereby the quantity $\frac{1000}{n} . \lambda_f$ of heat previously absorbed as heat of fusion is obtained again as heat of crystallisation, and the initial state is restored. The net result of the cyclic process is: A quantity of heat $\frac{1000}{n} . \lambda_f$ falls from the temperature T_0 to the temperature T_1; thereby an amount of work RT_0 is obtained. But according to the second law

$$\frac{\Delta A}{-Q} = \frac{\Delta T}{T}, \text{ therefore since } -\lambda_f = \lambda_{cr.}, \frac{RT_0 . n}{1000 . \lambda_{cr.}} = \frac{T_0 - T_1}{T_0};$$

$$T_0 - T_1 = \frac{RT_0^2}{1000 . \lambda_{cr.}} . n = K . n.$$

Here again K means the lowering of freezing-point when 1 mol is dissolved in 1000 gms. of solvent.

(4) *Association and Dissociation.*—The magnitude of the osmotic pressure and the vapour pressure lowering is determined simply by the molar concentration of the freely moving particles which the dissolved substance forms in the solvent in question. If the number of these particles is diminished by association or increased by dissociation, then in formulæ (3), (4) and (6), the number n becomes smaller or larger, and this causes a diminution or an increase in the lowering of vapour pressure, raising of boiling-point and lowering of freezing-point as compared with what would be expected from the normal molecular weight. The molecular weight will then be found to be larger or smaller than the normal value. For example, organic compounds containing hydroxyl or carboxyl show association (too high molecular weights) in organic solvents of small dielectric constant, such as benzene. Dissociation (and, accordingly, molecular weights which are too low), is found chiefly with electrolytes, that is with acids, bases and salts in solvents of large dielectric constant, and especially in aqueous solution.

The degree of dissociation α, i.e. the fraction of the substance in solution which is dissociated, can be calculated from the known theoretical molecular weight and the apparent molecular weight found: if the solution contains n mols of salt, there are $\alpha . n$ mols dissociated and $(1 - \alpha) . n$ mols undissociated. If by dissociation each molecule forms two ions, the solution contains altogether $(1 - \alpha) . n$ undissociated molecules $+ 2\alpha n$

ions $= (1 + \alpha)n$ particles. (If the dissociation is into x particles, there will be $(1 - \alpha) . n + x\alpha n = [1 + (x - 1)\alpha]n$ particles.)

Since the total weight of dissolved substance is fixed, n times the known molecular weight must be equal to $n(1 + \alpha)$ times the molecular weight found, or the known molecular weight $(1 + \alpha)$ times the molecular weight found:

$$\alpha = \frac{\text{known mol. wt.} - \text{mol. wt. found}}{\text{mol. wt. found}} \quad . \quad . \quad (8)$$

For dissociation into x particles:

$$\alpha = \frac{\text{known mol. wt.} - \text{mol. wt. found}}{(x - 1)\ \text{mol. wt. found}}.$$

It is now known that these considerations, which formerly were considered to be of general validity, should be applied in this form only to weak electrolytes, for which the position of the equilibrium which shifts with increasing dilution towards the side of the dissociated particles is practically the only factor which determines the deviation from the behaviour of undissociated substances.

On the other hand, for strong electrolytes such as strong acids and bases and many salts, a very large degree of dissociation is assumed at all concentrations; indeed for some time now it has been customary to speak of complete dissociation. Formerly, the deviations from proportionality to the concentration, of the changes of specific conductance, of osmotic pressure and of catalytic activity, in the case of strong electrolytes as well were referred to different degrees of dissociation at different concentrations. But more exact measurements have shown that at the same concentration the degree of dissociation calculated from conductivity measurements is somewhat different from that calculated from measurements of lowering of the freezing-point or raising of the boiling-point or from the catalytic activity of the ions. These discrepancies are now explained as being caused by the electrostatic forces which the ions exert reciprocally and upon the molecules of the solvent, and which affect the conductivity, the osmotic pressure and the catalytic activity somewhat differently. These forces are stronger, the higher the concentration and therefore the smaller the distance apart of the ions. With increasing dilution they became weaker, and at the same time the ions approach more closely the state in which they no longer influence each other, but behave as completely freely moving independent particles. This state is identical with that which had previously been assumed as the

state of complete dissociation at infinite dilution. The reduction in free mobility and activity undergone by the ions as a consequence of their mutual action arising from the electrostatic forces makes it appear that the concentration of free ions is less than that corresponding to the assumption of complete dissociation. The factor by which the ionic concentration corresponding to this assumption must be multiplied in order to obtain the concentration of non-mutually influencing ions which would show the same behaviour as that actually observed, is called the "osmotic coefficient," the "conductivity coefficient," or the "activity coefficient," as the case may be. The two latter can also be referred to as "the apparent degree of dissociation." The behaviour of any electrolyte solution containing ions of different kinds may (in dilute solution) be approximately calculated additively from the coefficients of the ions in question.

References :—
Eucken, Jette, and Lamer. §§ 139-145 ; 158 ; 182-193.
Nernst. Bk. I. Chap. V.
H. S. Taylor. Chap. VII.

(b) Experimental

The experimental problem consists in determining first the freezing- or boiling-point of the pure solvent, and then that of the solution—the latter at three different concentrations, which are obtained by successive introductions of tablets or of portions of the liquid of the substance to be investigated, into the solvent.

(1) Auxiliary Apparatus

(α) *The Beckmann Thermometer* (Fig. 3).—Since it is a question of the precise measurement of comparatively small *differences* of temperature (at most 3° to 4°) use is made of a so-called "Beckmann" thermometer with a variable filling of mercury and a range of scale of not more than 6°. It is divided into $^1/_{100}$°; with a lens $^1/_{1000}$° can be estimated. According to the amount of mercury in the bulb, this temperature interval of 6° corresponds to different actual temperatures. With freezing-point determinations, where a lowering occurs, the freezing-point of the pure solvent should lie well up on the scale—say between the graduations 4 and 6, in order that as much of the scale as possible may be utilised ; with boiling-point determinations, on the other hand, where there is a raising, the initial boiling-point should lie between 0 and 2.

Alteration of the amount of mercury is made possible by having a mercury reservoir (*f*) connected to the upper end of the thermometer capillary, which is bent twice at right angles. The adjustment of the amount of mercury is always most simply done as follows: the thermometer is held by the middle in the right hand, and turned upside down; it is then tapped once or twice (not too gently) at the back, at the level of the reservoir already mentioned, with the side of the left hand, near the first finger. The mercury in the reservoir then runs down, and remains hanging in the upper part when the thermometer is restored to its upright position. The thermometer bulb is now warmed with the hand or in a steam bath, according to need (for still higher temperatures an oil bath should be used, but *in no case should the bulb be heated over a free flame*). This is continued until the mercury thread rises up the capillary *c*, through the graduated portion *de*, and unites with the mercury in the upper reservoir. The thermometer bulb *ab* is now dipped into a bath at a temperature 2° to 3° above the freezing-point, or 6° to 7° above the boiling-point of the solvent to be used. After waiting about a minute, so that it is certain that the bulb has reached the temperature of the bath, the upright thermometer is tapped at the back in the manner prescribed; the excess mercury then breaks loose at the widening of the thermometer capillary, and falls into the lower part of the reservoir. The temperatures given for the bath are corrected by the length of the mercury thread between the upper end of the scale and the place where the mercury breaks away at the widening of the capillary in the reservoir; usually this corresponds to about two degrees on the scale, and the temperatures given are based on this assumption, bearing in mind the desired position of the freezing- or boiling-point on the scale (see above). Great care should be taken that no small droplets of mercury remain hanging in the immediate neighbourhood of the widening of the capillary in the reservoir; otherwise the effect is to cause an alteration of the original filling, and hence of the position of the freezing- or boiling-point, if in the course of a measurement, as may, for example, happen during the melting up of the frozen solvent, mercury from the capillary enters the upper part

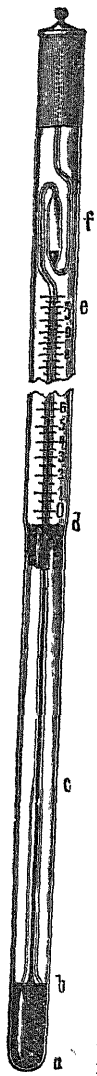

FIG. 3.

of the reservoir. *Care must be taken, when tapping, to avoid the use of any hard substance, such as wood or especially metal.*

Since the quantity of mercury in the bulb varies with the temperature for which it is set, 1° of the thermometer scale at different temperatures corresponds to different true temperature differences. At high temperatures, where the quantity of mercury in the bulb is small, an increase of temperature of more than 1° is required in order that the thread shall rise by one Beckmann degree; at very low temperatures it is less. Usually the scale is so calibrated that the *degree value* is correct for temperatures between 0° and 5° Centigrade. The degree values for lower and higher temperatures, based on the corrections for reduction to gas-thermometer readings and for exposed

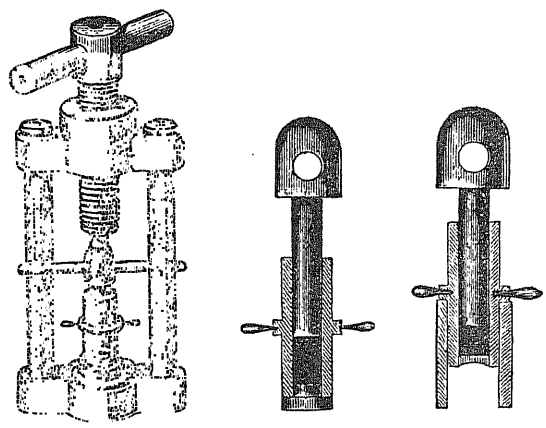

FIG. 4.

stem (see p. 86) (room temperature 18° to 22°), are tabulated below. The figures apply to a thermometer made of glass of type 16III and with the stem completely exposed.

Temperature Range.	Degree Value.
− 35° to − 30°	0·982
0° to + 5°	1·000
+ 20° to + 25°	1·009
+ 30° to + 35°	1·013
+ 45° to + 50°	1·020
+ 95° to + 100°	1·037
+ 145° to + 150°	1·050
+ 195° to + 200°	1·058
+ 245° to + 250°	1·060

The temperature differences directly observed must be multiplied by the appropriate degree value to obtain the actual

temperature differences which are to be used in the molecular weight calculation.

(β) *Tablet Press* (Fig. 4).—The substance to be used is finely ground in a mortar and made into the form of tablets in the press. In a freezing-point determination it is not advisable to use large crystals directly because they go into solution with much more difficulty than the pressed tablets which rapidly fall into a fine powder. The manipulation of the tablet press is as follows: the pulverised substance is introduced into the short strong-walled steel cylinder, the special stopper put in place, and the powder compressed by turning the screw. A second portion can be introduced by unscrewing and removing the stopper. When the tablet is large enough it is pressed out of the steel cylinder by placing the latter on top of the thin walled brass cylinder, so that the tablet falls into the empty space in this.

The first three or four tablets, which are always contaminated by rust, grease, or dirt, are thrown away. From among the clean ones, those of suitable size are selected (the approximate weight of a tablet which is suitable should be known beforehand) and kept in three weighing bottles with ground-in stoppers. These are weighed on an analytical balance accurately to 0·0001 gm. After using the tablet the weighing bottle is weighed again, empty. The different weighing bottles should be distinguished by lines or numbers to avoid their being interchanged. After use the tablet press should be carefully cleaned, and slightly greased to avoid rusting.

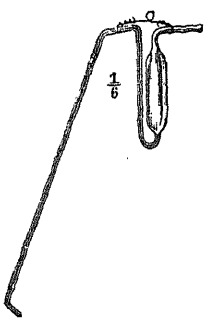

FIG. 5.

(γ) *Pipette for Introducing Liquid* (Fig. 5).—Liquids are drawn into a Beckmann pipette provided with a long extension, and weighed in it. The liquid is then injected through the extension into the solvent. For this purpose, in the boiling-point method, the Liebig condenser is not removed from the apparatus; the long extension makes it possible to introduce the liquid into the inside of the condenser below the zone of condensation.

(2) BECKMANN'S FREEZING-POINT METHOD.

(α) *Apparatus.*—The apparatus described by Beckmann is used (Fig. 6): The actual freezing vessel is a wide test-tube, A, with a side tube attached, through which the tablets are intro-

duced. The vessel is closed at the top by a plain bored cork in which the Beckmann thermometer is held. A second, somewhat wider test-tube, B, serves as an air jacket in which the lower part of the freezing vessel, as far as just below the side

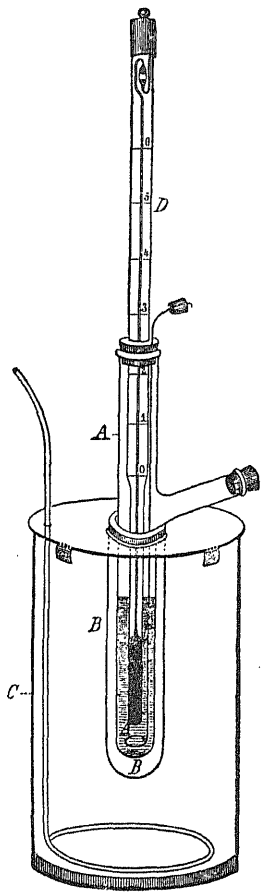

FIG. 6.

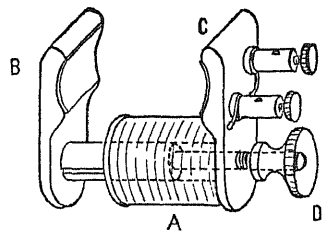

FIG. 7*a*.

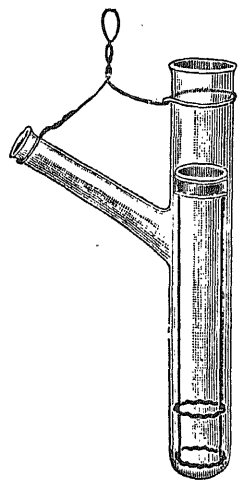

FIG. 7*b*.

tube, is placed. The air-jacket is fastened by means of elastic spring clamps to the metal cover of the wide glass cylinder, C, which serves as the cooling bath. The quantity of cooling mixture must be sufficient to surround the whole of the solution in A. Instead of stirring the solution in A by the small hand stirrer shown in Fig. 6, an electromagnetically operated stirrer (Fig. 7*b*)

may be used. On completing the circuit, the upper wide platinised steel ring is drawn up into the magnetic field of the poles, BC, of the electromagnet, A (Fig. 7*a*). The electromagnet is fixed to the freezing vessel above the side tube. Several layers of filter paper should be wrapped round the place where the electromagnet is to be clamped to the glass. The position of the magnet is adjusted so that the length of the "stroke" of the stirrer is about 1 cm. The periodic make and break of the current is effected by a metronome with the proper contact arrangements; the source of current is an accumulator. The lower end of the Beckmann thermometer should be about 1 cm. from the bottom of the freezing vessel; it must be exactly central, so that the lower narrow ring-shaped part of the stirrer does not strike or rub against it.

(*β*) *Details of the Experiment.*—(1) *With Benzene as Solvent.*—The freezing vessel is cleaned, carefully dried, closed at the top and at the side tube with corks, and weighed on a rough balance to $^1/_{100}$ gm. Pure dry benzene [1] is introduced into the apparatus to a height of about 7 cms., and the weight of solvent found by again weighing the tube closed with the same corks. The outer glass cylinder is filled with cold water and a few pieces of ice added, until the temperature after stirring has fallen to about $+ 3°$. Too low a temperature of the cooling bath (more than $1\frac{1}{2}°$ to $2°$ below the freezing-point of the solvent) is to be avoided, because then, owing to the rapid heat interchange between the freezing vessel and the cooling bath, the freezing-point may easily be found too low, and the more so the greater the difference in temperature between freezing vessel and cooling bath.

The freezing vessel is put into the air jacket, the Beckmann thermometer introduced, and the electromagnetic stirrer started. From time to time the outer bath is stirred well and its temperature adjusted. The thread of the Beckmann thermometer will be seen to sink slowly. In most cases the phenomenon of super-cooling will be met with; the thread, which has been falling gradually and uniformly, suddenly rises one or more tenths of a degree, and then, in the case of the pure solvent, remains constant for a long time at this maximum temperature. This sudden change of temperature shows that the previous super-cooling is being annulled; the highest temperature reached is the true freezing-point, where solid and liquid are in equilibrium. At the same time the formation of fine needles of solid benzene can be seen.

[1] Pure benzene dried over $CaCl_2$ and sodium, and distilled.

The first determination of all serves only to fix approximately the freezing-point of pure benzene. (Should it now appear that the thermometer is not correctly set, it must be removed and set again as already described. Since on taking it out loss of benzene is unavoidable, the weight of benzene must be determined again before the new measurement.) At least two determinations of the exact freezing-point must now be made. The freezing vessel is removed from the air-jacket, and the frozen benzene melted by the warmth of the hand; the experiment is then started again as before. (The temperature of the cooling bath must be controlled from time to time.) The fall of the mercury thread is followed until a position is reached about $^1/_{10}°$ above the freezing-point already provisionally fixed. From now on the thermometer is read every 20 seconds, always tapping it first with an empty thermometer case; the readings are made to $^1/_{1000}°$ with a lens. After the super-cooling is over, the highest temperature reached is the true freezing-point. If it does not remain constant for a considerable time, but gradually sinks by one or two hundredths of a degree, the solvent is impure. Owing to the freezing out of pure benzene, the concentration of the impurities in the liquid is raised, and the lowering of the freezing-point is increased. In this case the apparatus must be emptied out and again carefully cleaned. The measurement is repeated a second and third time, the benzene being just melted and the experiment carried out as above.

The next step is the introduction of the first tablet: the electric stirrer is stopped, the tablet dropped in through the side tube, and the stirrer re-started. It is best to take the freezing vessel out of the cooling jacket, and wait until the tablet has dissolved with the aid of the continuous stirring. It is then replaced in the cooling jacket and the falling of the thread watched carefully. In the first measurement, only the super-cooling and the highest temperature reached are noted. The repetition is begun at about $^1/_{10}°$ above the observed maximum temperature, and the exact temperature noted every 20 seconds, as described above, with pure benzene. In this case the temperature naturally does not remain at the highest point, but falls slowly for the reason mentioned in connexion with impure benzene. For the subsequent calculation, however, it is the maximum temperature which is important. The results should be recorded in the form of a clear scheme, from which the degree of super-cooling and the highest temperature reached can be seen at once. The experiment is repeated a second time. The maximum tempera-

tures must agree to within $^3/_{1000}°$ or $^4/_{1000}°$. If the super-cooling is about the same in each case, the mean is used in the calculation; with different amounts of super-cooling, the correction discussed later (p. 25) for the amount of solvent frozen out must be applied to each measurement individually. A second tablet is then dropped in, and treated like the first; here again the freezing-point is first provisionally, and then twice accurately determined. The procedure is repeated with the third tablet. When repeating the experiment, the temperature of the cooling bath should be adjusted to be about 1° to 2° below the freezing-point found provisionally in the preliminary experiment.

After the experiment the solution is poured into a bottle for benzene residues, and the freezing vessel cleaned immediately. *In all work with benzene the proximity of an exposed flame must be avoided.*

(2) *With Water as Solvent.*—The procedure here is exactly the same as with benzene, except that in most cases "seeding" with a small solid crystal is necessary, since the super-cooling can become very marked. The seeding is carried out as follows: a number of clean glass beads are put into a test-tube, two or three drops of distilled water added and shaken so that the beads are covered with a fine "skin" of water; by putting the tube into a freezing mixture this skin is frozen. The electromagnetic stirrer is stopped in the raised position, and the prepared glass bead dropped through the side tube into the liquid. Or a water-drop hanging on a glass capillary can be frozen by lowering it into a test-tube standing in a freezing mixture, and then scraped off against the raised stirrer. Once the freezing-point of ice has been determined, seeding should always be done when the super-cooling exceeds $^3/_{10}°$. In experiments with water, the freezing bath should not be colder than $-2°$. Too much salt should not be used to begin with, but the correct amount found by trial. The required temperature is maintained by occasional additions of small pieces of ice and of salt.

(3) *Failure of the electromagnetic stirrer.*—This can happen in various ways:—

Either the Beckmann thermometer is no longer exactly central, so that the stirrer strikes against it;
or the connecting wire is broken or a clamping screw is loose, so that the circuit is broken;
or the make-and-break is not functioning properly; it often happens that the contact spring is bent in such a way

that the contact is too short and is broken again before the stirrer has been raised high enough;

or there is a large amount of solid solvent crystallised out, so that the stirrer is held mechanically;

or the accumulator is discharged.

(γ) *Calculation of Results.*—This can only be done directly with measurements in which there has been no super-cooling, or very little. If the super-cooling exceeds 0·1° with benzene or 0·25° with water, the following correction for the solvent frozen out must always be made. The amount of solvent crystallised out stands in a simple relation to the degree of super-cooling: the quantity crystallising out is such that the heat of crystallisation set free is able to raise the temperature of the whole quantity of solution, and also the freezing vessel, stirrer and thermometer, in so far as they take part in the changes of temperature, from the lowest point of the super-cooling up to the true freezing-point. The heat of crystallisation of benzene is 30·4 cals. per gm., and that of water 80 cals. The specific heat of benzene is 0·41 cal. and of water 1 cal. The total heat capacity of the parts of the freezing vessel, stirrer and thermometer which came in question is estimated at about 16 cals. in the apparatus used. Hence, if G is the total weight of solvent, and G′ the weight of the part frozen out when the super-cooling amounts to $t°$,

$$\begin{aligned} &\text{with benzene } G' \,.\, 30{\cdot}4 = (G \,.\, 0{\cdot}41 + 16) \,.\, t°, \\ &\text{with water } \quad G' \,.\, 80 \quad = (G \,.\, 1{\cdot}00 + 16)t° \,. \qquad (9) \end{aligned}$$

The concentration of the solution then becomes $\frac{g \,.\, 1000}{G - G'}$. It can easily be seen by a rough calculation that with G = 30 gm. *ca.* the effect of not taking into account the super-cooling will be to cause an error of 1 per cent. in the concentration when the super-cooling is 0·2° with benzene or 0·5° with water.

There are two ways of calculating m. If T_0 is the freezing-point of the pure solvent, T_1, after introducing the first tablet of weight g_1, T_2 after the second tablet g_2, and T_3 after the third g_3, then m can either be calculated from each determination separately:

$$m_1 = K \,.\, \frac{g_1 \,.\, 1000}{G \,.\, (T_0 - T_1)}; \quad m_2 = \frac{g_2 \,.\, 1000}{G \,.\, (T_1 - T_2)}; \quad m_3 = \frac{g_3 \,.\, 1000}{G \,.\, (T_2 - T_3)},$$

or one can add together the separate portions and combine the result with the corresponding total freezing-point lowering:

$$m_1' = K \cdot \frac{g_1 \cdot 1000}{G \cdot (T_0 - T_1)}; \quad m_2' = K \cdot \frac{(g_1 + g_2) \cdot 1000}{G \cdot (T_0 - T_2)};$$

$$m_3' = K \cdot \frac{(g_1 + g_2 + g_3) \cdot 1000}{G \cdot (T_0 - T_3)}.$$

If the substance is one which neither associates nor dissociates, then in the absence of any gross error the results of all the measurements, calculated by both methods, will agree within the experimental error. But if an error creeps in anywhere, then, according to where the error is, either the first or the second method of calculation will give results in better agreement. For example, if the freezing-point of the pure solvent has not been correctly determined, then by the first method this only invalidates the value of m calculated from the first experiment, and is without influence upon m_2 and m_3. By the second method, on the other hand, all three results are affected, although each successive one to a lesser extent. If the error is in the determination of T_1, by the first method this affects m_1 and m_2, and by the second method only m_1'. If the error is in the weighing of a tablet, by the first method the effect is limited to the portion in question, while by the second all those which follow are involved, though to a diminishing extent. Accordingly if the agreement in the values of m is bad when the experimental data are calculated by one of the methods, then the calculation should be made by the other method as well. By considerations such as these it is often possible to discover the probable cause of the error.

A "drift" of the separate values for the molecular weight, in the sense that the molecular weight rises with increasing concentration, may sometimes be due to increasing polymerisation of the solute; a drift in the opposite sense would require increasing dissociation, i.e. decomposition. The drift is in this case more marked when the calculation is made by the first method than by the second.

(3) Rast's Micro-method of Molecular Weight Determination

As a solvent molten camphor is used. Camphor has a very high molecular lowering of the freezing-point: 49·8 as against 5·12 for benzene and 1·86 for water. Consequently it is possible to measure the lowering of the freezing-point of solutions of moderate concentration in an ordinary melting-

point apparatus, using a thermometer graduated in whole degrees, which is read with a lens to $^1/_{10}°$.

The solution is prepared by mixing about 10 mg. of the substance under investigation with ten times the quantity of camphor (both weighed on an analytical balance accurately to $^1/_{10}$ mg.), and heating the mixture carefully to fusion, in a small test tube. The clear melt is allowed to solidify, ground up in a mortar and introduced into a thin-walled melting-point tube to a height of about 1 mm. The melting-point is then determined in the usual way in the ordinary apparatus. The difference from the melting-point of pure camphor determined in the same way is introduced into formula (7) already given.

The limit of accuracy of the method is about $\pm$ 5 per cent.

The method is not applicable to substances which decompose at the melting-point of camphor (174°), or react chemically with camphor.

(4) The Boiling-point Method

(α) *Swietoslawski's Method.* (1) *Apparatus.*—The new apparatus of Swietoslawski is used, the construction of which has the advantage that the thermometer is entirely removed from the direct action of the flame, and at the same time there is very intimate mixing of liquid and vapour. The actual boiling vessel S (Fig. 8) stands on an asbestos wire gauze and is heated from below by means of a flame. It terminates at the top in a 5 mm. tube R, which, after a right-angle bend opens through a jet D into a 3-cm. wide cylindrical glass vessel G; into this protrudes the lower part of a Beckmann thermometer, held by a cork. To this cylindrical vessel is connected another 5 mm. tube, which completes the connection with the

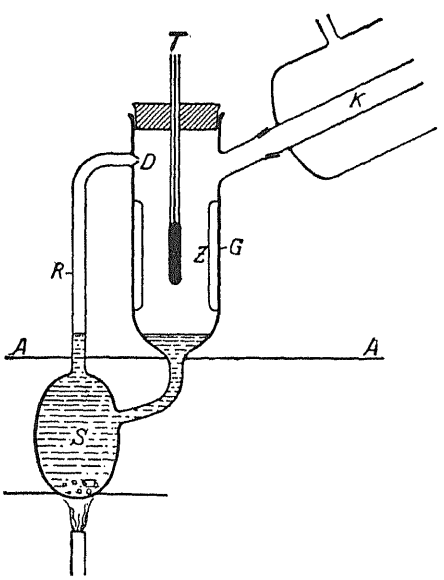

Fig. 8.

boiling vessel. To protect the thermometer from radiation from outside, there is inside G a cylinder Z, open at the top and bottom, about 6 cm. long and about 3 mm. less in diameter than G, in which it is held concentrically by glass points. Opposite to the jet D a short sloping Liebig's condenser K is attached by means of a ground joint, to condense the ether vapour. In order to avoid loss of ether as far as possible, a spiral condenser is connected on as well; in addition, the cooling water is kept at as low a temperature as possible by passing it through a spiral of lead tubing in a freezing mixture. To protect the thermometer from direct radiation from the sides of the heating flame, a 10 cm. square asbestos shield A is placed above the boiling vessel; the shield is made of two small sheets of asbestos placed one above the other with slits for the two tubes.

(2) *Details of the Experiment.*—The apparatus is thoroughly cleaned and dried and at the same time about thirty or forty well cleaned and dried garnets are placed in the boiling vessel S to prevent the boiling being delayed. (At perfectly smooth, gas-free surfaces, the first bubbles of vapour are formed in the liquid only after a considerable degree of super-heating above the boiling-point. The rough surface of garnets, fragments of porcelain, platinum clippings or small platinum tetrahedra, at which considerable quantities of gases are adsorbed, facilitates bubble formation and therefore tends to prevent super-heating and delayed boiling in a way similar to the way in which crystals in a supersaturated solution act as crystallisation nuclei and facilitate precipitation of the solid phase.) The apparatus is then weighed on a rough balance to $^1/_{100}$ gm., for which purpose the wide opening (through which the thermometer is introduced later) and the joint of the condenser are closed by suitable corks. Pure dry ether is now poured into the apparatus until it stands about 2 cm. up the tube R. The weight of the solvent is found by a second weighing. Then the Beckmann thermometer, already in a one-hole stopper, is put in position, and the condenser K is put into the ground joint, both as quickly as possible, to avoid loss of ether. The lower end of the thermometer bulb must be about 2 cm. down the cylinder Z and at least 2 cm. above the ether level. After putting on the spiral condenser and turning on the cooling water, the barometer is read and the heating begun. As soon as the ether is boiling freely a rapid stream of vapour bubbles, separated by layers of the liquid, rises up the tube R. The liquid in a state of fine division and intimate mixture with the vapour is thus sprayed

into the thermometer bulb from the fine jet D. The heating must be strong enough to keep a continuous stream of liquid and vapour over the thermometer bulb. The flame should be protected by a suitable shield from draughts. The time at which boiling begins is recorded (this is required for the calculation of the apportioning of the final loss of ether, see later), and after gentle tapping with an empty thermometer case the position of the mercury thread is read to the nearest $^1/_{1000}°$ with a lens. The boiling is continued for another ten minutes, the temperature being read and noted every minute. The position of the thread should not alter by more than $^2/_{1000}°$ or $^3/_{1000}°$. The outer spiral condenser is now removed and the first tablet dropped into the Liebig condenser; it will be immediately washed down by the condensing ether. If the tablet remains sticking above the zone of condensation, it is pushed farther down by a glass rod. The spiral condenser is then replaced. After five minutes the reading of the thermometer is noted again, and its constancy checked for a further ten minutes, as above. *It is important, in this method, not to interrupt the boiling or to moderate it by lowering the flame.* Alterations in the size of the flame affect the observed boiling-point by several thousandths of a degree, probably because thereby the speed of the ether circulation is altered, and therefore also the heat exchange with the surroundings. Also, if the heating is irregular the loss of ether subsequently determined cannot be regarded as uniformly distributed over the whole experiment.

The second and finally the third tablets are dropped in, noting in each case the time at which it is introduced; the corresponding boiling-points are determined, as with the first, and their constancy carefully checked.

At the end of the experiment the barometer is read and the apparatus allowed to cool; the thermometer and condenser are removed and the openings closed by the proper corks. The loss of ether, if any, is determined by another weighing; it can be assumed to have taken place uniformly over the whole period of the boiling. In calculating the concentrations, a correction must be made for the amount of ether lost up to the time at which the tablet in question was dropped in.

The used ether is poured into a bottle for ether residues, and not down the sink. The boiling vessel is carefully cleaned.

(β) *Beckmann's Method.* (1) *Apparatus.*—The actual boiling vessel (Fig. 9) consists of a wide test-tube with two side limbs, in which reflux condensers are put by means of joints or corks, so as to be gas tight. The upper opening is closed by a cork

through which the Beckmann thermometer passes to a level such that the thermometer bulb is completely immersed in the boiling liquid. In the lower part of the boiling vessel are garnets or glass beads to a height of 2 or 3 cm., to diminish the delay in boiling. The boiling vessel up to the side tubes is surrounded by a double-walled cylindrical glass jacket, into which through the short side tube are placed garnets together with as much of the solvent to be used as is required to make the levels of the liquid in the boiling tube and in the outer jacket approximately the same. During the experiment a reflux condenser is attached to this side tube. The whole apparatus is placed upon an asbestos wire gauze and heated by means of a

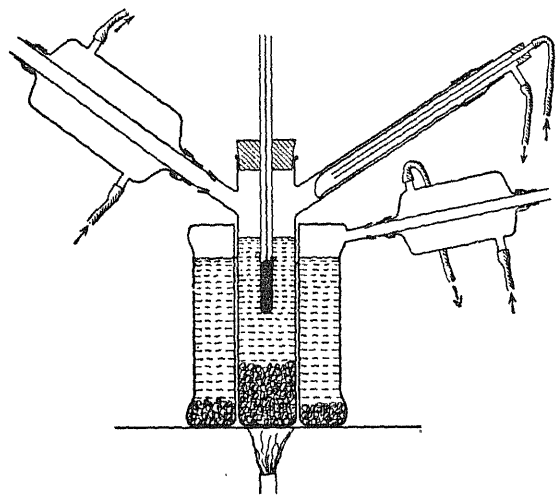

FIG. 9.

flame shielded from draughts, of such a size that the liquid both in the outer jacket and in the inner boiling vessel is brought into turbulent ebullition, and remains so during the whole experiment; otherwise there is not sufficient mixing of vapour and liquid, and the boiling-point observed will be wrong or unsteady. To obtain sufficient cooling when low-boiling solvents are used (e.g. ether), the cooling water must first be lead through a spiral of lead tubing lying in a mixture of ice and water.

(2) *Details of the Experiment.*—These correspond completely with those described under (α), page 28. The tablets are inserted by removing the Liebig condenser attached to the side limb.

(γ) *Calculation of the Results.*—This is done by the two methods given on page 25. The multiplication of the observed temperature difference by the degree value (Table on p. 19) must not be omitted. Neglect of this correction means, in the case of ether, an error of more than 1 per cent.

If a large change in the height of the barometer has taken place between the determination of the boiling-point of the pure solvent and those of the solutions, a corresponding correction must be applied to the boiling-point of the pure solvent. For water this can be done very easily by means of the Table on page 35 by interpolation. But it can also be done for any solvent in the following way: let p be the original height of the barometer, Δp the alteration in question, M the molecular weight, Λ the molar heat of condensation, and K the molar boiling-point raising of the solvent; then according to the Clausius-Clapeyron equation there exists the following relationship between the alteration of the height of the barometer, and therefore of the pressure under which the liquid is boiling, i.e. of the vapour pressure of the liquid when boiling, and the change ΔT of the temperature of boiling:

$$\frac{\Delta p}{p \,.\, \Delta T} = \frac{\Lambda}{RT^2} = \frac{M}{K \,.\, 1000} \text{ (see p. 11)}$$

$$\Delta T = \frac{\Delta p}{p} \,.\, \frac{K \,.\, 1000}{M} \quad . \quad . \quad . \quad . \quad (10)$$

A rise in the barometer height of Δp corresponds to a rise in boiling-point of ΔT.

(c) Accuracy of the methods

It has already been shown in the introduction (p. 2) that in a molecular weight determination by the cryoscopic or the ebullioscopic method the least accurate part of the determination is the value of ΔT. As was shown there, even with the most careful working, in consequence of the variability of the position of the thread with the strength of the tapping, and because of the uncertainty in estimating thousandths of a degree, this measurement is affected by an error of from 1 to 2 per cent. The total accuracy of an ordinary molecular weight determination amounts, therefore, at best to 1 to 2 per cent., even when the corrections for the freezing out of solvent as a result of supercooling (p. 25) or the loss through evaporation (p. 29), and for

the variable degree value and the exposed stem of the thermometer (p. 19) have been taken into account. If the introduction of these corrections is omitted, as is often done, the accuracy amounts at best to 3 to 5 per cent. With high-boiling solvents an error of even 10 per cent. may occur. (Neglect to correct for the degree value alone, at temperatures over 200°, causes an error of about 6 per cent.)

II. VAPOUR PRESSURE AND DISTILLATION OF LIQUID MIXTURES

A. NON-MISCIBLE LIQUIDS. DETERMINATION OF THE MOLECULAR WEIGHT OF A LIQUID

(a) Theory

A CHEMICALLY homogeneous solid or liquid substance possesses at every temperature a definite vapour pressure. The dependence of vapour pressure upon temperature is represented graphically by the "vapour pressure curve." If there are two liquid components in a closed space, then the total pressure is equal to the sum of the partial pressures, and these differ more or less from the vapour pressures of the pure substances, depending upon the reciprocal solubilities of the liquids and the solubilities of their vapours in the liquids. The simplest case is that of liquids with which the liquid phases are not appreciably soluble in each other. Each of the two liquids then has the same vapour pressure curve as the pure substance alone. The total vapour pressure over the liquid mixture is equal to the vapour pressures of both components added together. The vapours are always miscible in all proportions. Boiling begins when the sum of the vapour pressures is equal to the external pressure acting upon the system.

(1) This relationship underlies the process of "distillation in steam." Considering, for example, a mixture of water and nitro-benzene, then according to the gas laws, the relative molar quantities of the two components present in the vapour space are as their partial pressures. Under an external pressure of 1 atmosphere the mixture boils at 99°. The partial pressure of water then amounts to about 74 cm. and that of nitrobenzene to about 2 cm. The molar quantities in the vapour space are therefore in the proportion of 37 : 1. If the vapour is condensed the distillate will contain 37×18 gms. water to 123 gms. nitrobenzene. Thus in spite of its small partial pressure the fraction of nitrobenzene in the distillate is considerable (about 16 per cent. by weight), because the molecular weight is very

much greater than that of water. Steam distillation can therefore always be applied with advantage to a high boiling compound which is non-miscible with water, if it possesses a noticeable vapour pressure at 100° and a molecular weight much greater than that of water.

(2) The molecular weight M_x in the vapour state of one of the components can be determined when the molecular weight M and the vapour pressure curve of the other component are known. Let P be the barometric pressure under which the mixture is boiling at say $t°$, and p the vapour pressure of the second component at this temperature (taken from the vapour pressure curve); let g_x and g be the quantities of the two substances in the vapour, which are readily determined by analysis of the distillate. Then if n_x and n are the mol. numbers,

$$\frac{g_x}{g} = \frac{n_x \cdot M_x}{n \cdot M};$$

$$\frac{n_x}{n} = \frac{P - p}{p};$$

$$M_x = M \cdot \frac{g_x \cdot n}{g \cdot n_x} = M \cdot \frac{g_x p}{g(P - p)} \quad . \quad . \quad (11)$$

(b) Experimental

The molecular weight of a liquid which is not miscible with water is to be determined.

(1) *The Apparatus.*—The apparatus used (Fig. 10) is similar to that ordinarily used in steam distillations, except that one of the flasks has an attachment at the side which is filled with glass beads, to cause a more intimate mixing of the two liquids which condense there, so that both liquid phases are always in contact with the vapour phase, and exert their full vapour pressure. For determining the temperature a Beckmann thermometer is used, which is set so that the boiling-point of pure water lies between the degree marks 4 and 6 (see p. 17). The distillate is collected in a 100 c.c. measuring cylinder.

(2) *Procedure.*—First the boiling-point of pure water is measured on the Beckmann thermometer ($= t_1'$). For this purpose the right-hand flask is used, the neck being closed by a cork. The barometric height is read, the water heated to vigorous boiling and the thermometer read with a lens, after tapping it at the back, opposite to the place where it is to be read, with a glass rod covered with rubber or an empty thermometer case. The vapour can be allowed to escape into the

free air, without a condenser. The reading must remain practically constant for ten minutes. The water is then poured out and the liquid to be investigated by steam distillation is put into this flask to a height of about 2 cm. The apparatus is put together as in Fig. 10. The water in the left-hand flask is simply boiled vigorously; a small flame is left burning under the right-hand flask to assist the heating by the heat of condensation of the water. About 30 c.c. are distilled off before the measuring cylinder is placed under the condenser. During

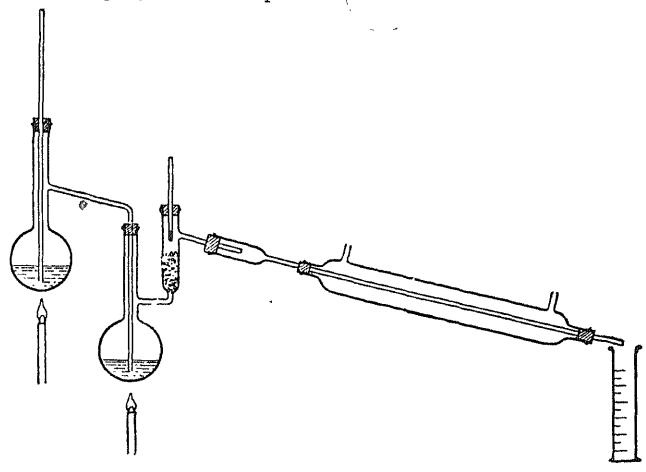

FIG. 10.

the distillation the temperature of boiling is read from time to time ($= t'_2$); it must remain constant to within $^1/_{100}°$ or $^2/_{100}°$. After about 50 c.c. have been collected, the experiment is stopped. The separation of the two liquids in the measuring cylinder is accelerated by gentle tapping. Finally the barometer is read again.

(3) *Calculation.*—The vapour pressure of water in the neighbourhood of 100° may be taken from the following table:

94·0°	610·9 mm.	98·0°	707·3 mm.
95·0°	633·9 ,,	99·0°	733·2 ,,
96·0°	657·6 ,,	100·0°	760·0 ,,
97·0°	682·1 ,,	—	—

These pressures apply to a barometer of which the mercury column and the scale are at 0°. The barometric height as read as $t°$ must therefore be corrected to 0°. This is done by means of the formula

$$P_0 = P[1 - (0{\cdot}0001817 - \beta) \,.\, t].$$

t is the temperature of the barometer, read on a small thermometer in the immediate neighbourhood of the barometer; 0·0001817 is the coefficient of expansion of mercury, β that of the scale. For glass $\beta = 0{\cdot}000008$, for brass 0·000018.

By means of the table given above a vapour pressure curve is drawn out on millimetre paper. (Abscissæ t, ordinates vapour pressure.) From this curve is taken the boiling temperature of pure water (t_1) corresponding to the reduced barometric height P_0. To this corresponds the reading t_1' on the Beckmann thermometer. The boiling temperature of the mixture is obtained by subtracting from t_1 the temperature difference $t_1' - t_2'$ after multiplication by the degree value at 100° (=1·037, see p. 19). The water vapour pressure p corresponding to this temperature t_2 is taken from the vapour pressure curve. g_x and g are found by multiplying the volumes in the measuring cylinder by the corresponding specific gravities. The specific gravity of water is taken from the Tables of Physical Constants; that of the liquid which is being studied can be found with sufficient accuracy by means of a hydrometer. Substitution of all these data into formula (11) leads to the molecular weight M_x of the liquid. Mainly because of the uncertainty in the determination of g_x and of g the accuracy of the method scarcely exceeds 5 per cent.

B. MISCIBLE LIQUIDS. CONSTRUCTION OF DISTILLATION DIAGRAMS

(a) Theory

The relationships in the distillation of miscible liquids are much more complicated than with non-miscible liquids. In the following discussion we shall consider only the case of complete miscibility, in which the components are soluble in one another in all proportions. The behaviour of such mixtures on distillation is most easily seen with the aid of curves; these express *either* the vapour pressure of the mixture at constant temperature as de-

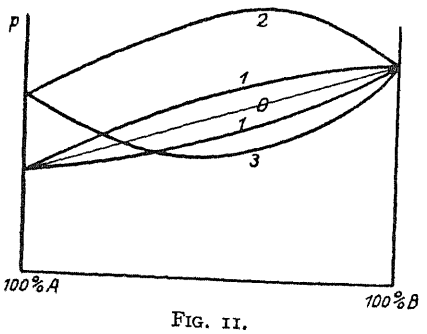

FIG. 11.

pendent upon the molar percentage composition, *or* the corresponding relationship between boiling temperature and composition. Fig. 11, in which boiling temperature is plotted against composition, illustrates the three possibilities of most importance: (1) the boiling-points of all mixtures lie between the boiling-points of the pure components (curves 0 and 1). (2) There are mixtures of higher boiling-point than either of the two pure components (curve 2). (3) There exist mixtures of lower boiling-point than either of the components (curve 3). In cases (2) and (3) the curve shows a maximum or a minimum.

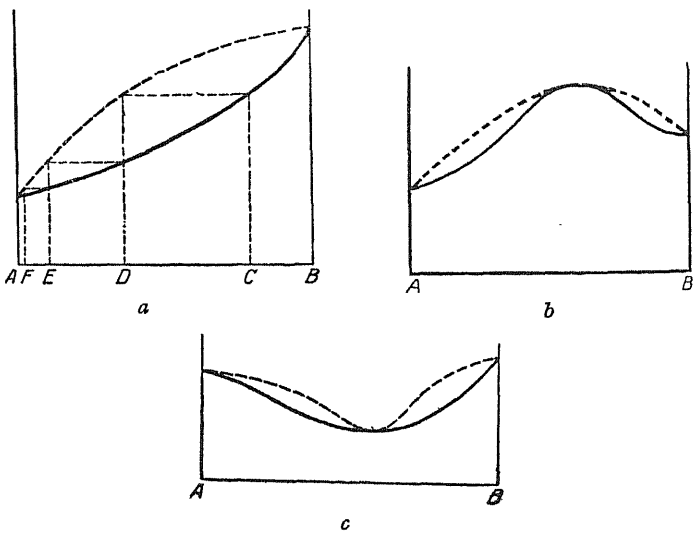

FIG. 12.

The mixtures of highest or lowest boiling-point are characterised by special properties, as will be seen by the following discussion.

Of the greatest importance for the behaviour of mixtures or distillations is the fact that the vapour (except in the mixtures corresponding to the maximum or minimum) has always a different composition from the liquid from which it arises. In Figs. 12 (*a*), (*b*), (*c*), in addition to the boiling-point curves which give the composition of the liquid corresponding to each temperature, there are given also the (broken line) curves which express the corresponding compositions of the vapour.

To find the composition of the vapour of a definite liquid mixture (e.g. C) a line is drawn from this point on the boiling-point curve parallel to the abscissa-axis to the nearest point

at which it cuts the broken curve. Thus, as Fig. 12*a* shows, a liquid of composition C develops a vapour of composition D. Since this is relatively much richer in A than the liquid, the composition of the latter must shift in the sense of a decrease in A and a relative increase in B, i.e. towards the right, or the high-boiling side. Since in the course of distillation the boiling-point, if it is not constant, can only rise, it follows that the composition of the vapour which leaves must be such that the composition of the liquid is shifted during the distillation towards the side of higher boiling-point. In the case (*a*) the final *distillation residue* which remains is a certain amount of pure B; in case (*b*) it is the mixture of maximum boiling-point, whether the composition of the initial mixture lies to the left or the right of the maximum; in case (*c*) according to whether the original mixture has a composition lying to the left or to the right of the minimum, the residue consists of pure A or of pure B.

If in the course of distillation the vapour developed from, say, the mixture C, of composition D, is condensed completely and the condensate of the same composition D is partially vaporised, then it gives rise initially to a vapour of composition E, which when condensed and again partially vaporised, produces vapour of composition F. If the process of condensation and partial evaporation of the condensate is repeated sufficiently often, there is finally obtained, in case (*a*) a distillate of the pure component A, in case (*b*) pure A or pure B according to the original composition of the mixture, and in case (*c*) the mixture with the lowest boiling-point. The mixtures with the highest and lowest boiling-point, are characterised, as the figures show, by the fact that the vapour developed has the same composition as the liquid. Since their composition is unaltered, these mixtures boil at a constant temperature like a pure substance. They differ from the latter in that their composition depends upon the pressure at which the distillation is done.

The repeated condensation and distillation discussed above is realised most simply, and as a continuous process, by the use of a distilling column, in which the desired action is brought about by means of a series of expansions and constrictions, or by filling with glass beads. By its use it is possible to break up any mixture: in case (*a*) into the two pure components, of which one is found in the residue and the other in the distillate; in case (*b*) according to whether the initial composition lies to the right or the left of the maximum, into a distillate of pure B or pure A, and a distillation residue consisting of the constant boiling mixture of highest boiling-point; in case (*c*) into the

constant boiling mixture of lowest boiling-point as distillate, and, depending upon the original composition, a residue of pure A or pure B.

Examples of (*a*) are mixtures of benzene + glacial acetic acid, benzene + chlor-benzene, oxygen + nitrogen. Case (*b*) is represented by acetone + chloroform, and the aqueous solutions of HCl, HBr, HI, HNO_3, HCOOH; case (*c*) by toluene + glacial acetic acid, carbon disulphide + acetone, water + ethyl alcohol, water + propyl alcohol.

References :—
Eucken, Jette, and Lamer, §§ 158-164 ; 174.
Reilly, Rae, and Wheeler. Chap. XIII.
Nernst, pp. 115-119 ; 566-573.

(b) Experimental

Four different mixtures (20, 40, 60, 80 mols per cent.) are made of each of the following pairs of liquids : benzene and glacial acetic acid, acetone and chloroform, toluene and glacial acetic acid ; the boiling-points of these mixtures are determined, and also the composition of the vapour which escapes from them. With these data the curves representing boiling-point and vapour composition as dependent upon the molar proportions of the liquid components in the mixture are constructed.

(1) *Apparatus.*—The measurements are made in an apparatus for molecular weight determination (Swietoslawski's form, cf. p. 27). The special boiling vessel holding from 10 to 15 c.c. is filled completely, so that the liquid stands about 1 cm. up the vertical tube. The small boiling flask is heated on an asbestos wire gauze with a micro-burner. To avoid too much cooling it is surrounded up to about half-way by an asbestos shield. The temperature is read to $\frac{1}{5}°$. The condenser is arranged so that it can be turned round (Fig. 13), so that on the one hand the boiling-point of the mixture can be determined whilst refluxing, and on the other hand, by turning down the condenser a small quantity of the liquid can be distilled off, for a determination of the composition of the vapour by analysis of the condensate.

(2) *Details of the Experiment.*—The boiling-points of the pure components under the existing barometric pressure are determined as described. The specific gravities are measured by means of hydrometers. Then the boiling-point curves of the three liquid pairs mentioned above are constructed; 20 c.c. samples of each of the four mixtures of each combination are

prepared, by calculating from the densities the proper volumes, and running these from a burette into the small boiling flask. The boiling-points are then determined, and expressed graphically in their dependence upon the composition. (Abscissæ: molar percentages; ordinates: boiling-points); in this way the boiling-point curves are obtained at the barometric pressure prevailing. In each case after determining the boiling-point the condenser is turned round and ½ c.c. distilled into a small glass tube which

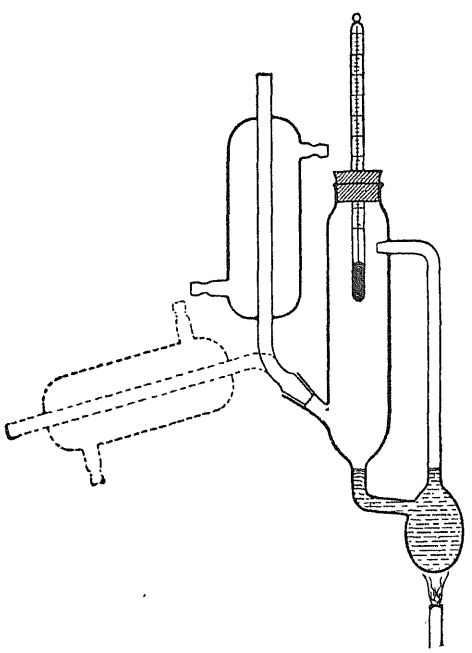

FIG. 13.

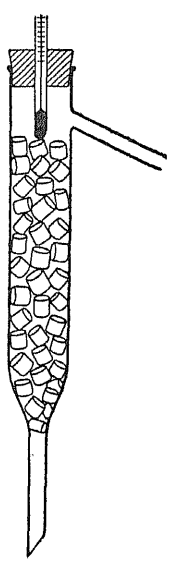

FIG. 14.

can be closed. The tubes are marked with the number of the experiment and kept for analysis later.

The analysis is done refractometrically. The refractive indices of the pure components and of the mixtures of which the boiling-points have been determined are measured with an Abbé or a Pulfrich refractometer (pp. 132 and 128). To obtain a sufficiently accurate curve of the refractive indices, it is sometimes necessary to prepare a few more intermediate mixtures. By plotting the refractive indices (or the angles as read directly) against the molar percentage composition, and drawing a curve through the points, the composition of the

distilled samples can easily be determined. All these refractometric measurements must be carried out as nearly as possible at the same temperature (room temperature is best).

On the basis of this investigation there can now be plotted on the boiling-point graphs the composition of the vapour at the boiling temperature, as well. In this way the two curves analogous to those in Fig. 12 (*a*), (*b*), (*c*), are obtained which throw light upon the behaviour of the mixture upon distillation.

One can verify the action of the distilling column described above by carrying out a fractional distillation, starting with 50 per cent. molar mixtures of the three liquid pairs taken before. The distilling column is of the form shown in Fig. 14; the wide part is about 10 cm. long and is filled with Raschig rings. In case (*a*) benzene and acetic acid are separated, in (*b*) and (*c*) a constant boiling mixture and the component which is in excess. The presence of a constant boiling mixture in the residue in the first case, and in the distillate in the second, and also their compositions, are found by measuring the refractive index of the condensed vapour and of the corresponding liquid.

III. SURFACE TENSION OF LIQUIDS

(a) General Theory

A LIQUID, when not acted upon by any external forces, takes the form of a sphere, that is, the form in which a given volume has the smallest surface; it is concluded from this that the surface has a tendency to diminish spontaneously, and consequently that its increase involves an expenditure of work. This tendency to decrease the surface is denoted by the "surface tension" σ and is measured by the work which must be expended in order to increase the surface by 1 sq. cm.

$$\text{Work} = \text{Surface tension} \times \text{change in surface.}$$

$$\text{Dimensions of surface tension} = \frac{\text{work}}{\text{surface}}$$

$$= \frac{m \,.\, l^2 \,.\, t^{-2}}{l^2} = m \,.\, t^{-2}.$$

This conception of surface tension can be very well illustrated with the aid of a small wire frame ABCD (Fig. 15), of which one side CD is movable, and into which a liquid film is brought. If the tendency of the surface to contract is just held in equilibrium by the weight G, and if the surface is extended through a slight increase in G, just so far that the side CD takes up the position C′D′, then work must be done against the surface tension equal to the surface tension multiplied by the newly-formed surface:

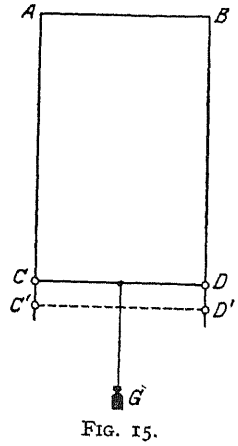

FIG. 15.

$$A = \sigma \,.\, 2 \,.\, (CD \,.\, CC').$$

The factor 2 is introduced because both the front and back surfaces of the film are extended. It is obvious from the figure that the force represented by the weight G is proportional on the one hand to the magnitude of

the surface tension, and on the other to the strip CD along which the surface is extended, so that the surface tension is equal to a force divided by a length. From this it follows that the dimensions of σ are

$$\frac{\text{force}}{\text{length}} = \frac{m \,.\, l \,.\, t^{-2}}{l} = m \,.\, t^{-2}.$$

One can also imagine the amount of work A necessary for the extension as being divided up in such a way that on each side of the film a force σ . CD must be overcome through a distance CC′.

The dependence of surface tension upon temperature is small. σ decreases with rise in temperature for all liquids, usually linearly. At about 6° to 8° below the critical temperature the surface tension becomes = 0. We have therefore the relationship

$$\sigma_t = k(\mathrm{T}_c - 6 - t),$$

in which T_c is the critical temperature, and k is a constant characteristic of each liquid. Suppose now that molar quantities of different liquids are compared by considering 1 mol in the form of a cube: Volume $= \frac{\text{Mol. wt.}}{\text{Density}}$; Length of one edge of the cube $= \sqrt[3]{\frac{\text{Mol. wt.}}{\text{Density}}}$. Then on multiplying the surface tension by the surface area of one side of this cube $\left(\text{which is nearly a constant for any particular liquid: area of one side} = \sqrt[3]{\left(\frac{\text{Mol. wt.}}{\text{Density}}\right)^2}\right)$ the relationship holds:

$$\sigma_t \,.\, \sqrt[3]{\left(\frac{\text{Mol. wt.}}{\text{Density}}\right)^2} = \mathrm{K} \,.\, (\mathrm{T}_c - 6 - t) \quad . \quad . \quad (12)$$

in this, K is now found not only to be approximately constant for a definite liquid at different temperatures, but for many liquids approximately the same value of about 2·1 is obtained (Eötvös' rule). The quantity K has therefore the significance of the temperature coefficient of the molar surface energy, and its constancy with numerous liquids forms an analogy to the constancy of the gas constant $\mathrm{R} = \frac{pv}{\mathrm{T}}$, which can be regarded as the temperature coefficient of volume energy. With water and with a series of oxygen-containing organic liquids (carboxylic acids,

oximes, ketones, aldehydes, alcohols, K is smaller and variable. The normal value is arrived at if the area of the side of the mol. cube, and accordingly the molecular weight, is increased; this can therefore be taken as evidence for polymerisation in the liquid state.

At 18° the surface tension measured in C.G.S. units is:

for water . .	. 72·8	Dyne cm.$^{-1}$
„ ethyl alcohol .	. 22	„ „
„ glycerine .	. 66	„ „

(b) Methods available for the measurement of surface tension

(α) *By the Breaking of a Film.*—The tension under which a liquid film just breaks, is determined. The determination is usually carried out as follows: a platinum plate or a platinum wire frame is tared on an analytical balance, and then the lower edge of the plate or the lower horizontal side of the frame is brought into contact with the surface of the liquid; on gradually loading the other scale pan a liquid film is drawn up. At a definite maximum load the thin film breaks and the wetted edge or side is dragged out of the liquid. The surface tension is found in absolute measure (dyne/cm.) by dividing the added weight in grams by twice the length of the edge dipped in (measured in cm.), and multiplying the quotient by 981.

This method is the most suitable for *absolute* determinations. It is made simpler and more convenient by the use of a torsion balance.

(β) *Measurement of the Rise in Capillaries.*—When a liquid rises up a capillary, the force which draws it up is equal to the surface tension σ multiplied by the length of the line of contact at which it adheres (Fig. 16); the weight of the column of liquid which is raised up tends to draw it downwards. When the liquid reaches its maximum height, the two forces are in equilibrium. If r is the radius of the capillary, h the height of rise (both measured in cm.), s the density of the liquid, and g the acceleration due to gravity, then

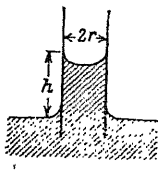

FIG. 16.

$$2\pi \cdot r \cdot \sigma = r^2\pi \cdot h \cdot s \cdot g.$$

The absolute value of σ is therefore

$$\sigma = \frac{r \cdot h \cdot s \cdot g}{2} \quad . \quad . \quad . \quad (13)$$

If for two liquids the heights of rise in the same capillary and the densities are measured, then

$$\frac{\sigma_1}{\sigma_2} = \frac{h_1 s_1}{h_2 s_2}; \quad \sigma_2 = \sigma_1 \frac{h_2 \cdot s_2}{h_1 \cdot s_1} \quad . \quad . \quad . \quad (14)$$

The level of the outer liquid is difficult to determine with accuracy, but this difficulty is got over in relative measurements, such as these by using two capillaries of different widths (r' and r''). Then for the first liquid

$$h_1' = \frac{2 \cdot \sigma_1}{r' \cdot s_1 \cdot g}; \quad h_1'' = \frac{2 \cdot \sigma_1}{r'' \cdot s_1 \cdot g};$$

so that $$h_1' - h_1'' = \frac{\sigma_1}{s_1} \cdot \frac{2}{g} \cdot \left(\frac{1}{r'} - \frac{1}{r''}\right) = \frac{\sigma_1 \cdot K}{s_1}.$$

Similarly for the second liquid $h_2' - h_2'' = \frac{\sigma_2 K}{s_2}$.

Therefore

$$\frac{\sigma_1 \cdot s_2}{\sigma_2 \cdot s_1} = \frac{h_1' - h_1''}{h_2' - h_2''}; \quad \sigma_2 = \sigma_1 \cdot \frac{s_2 \cdot \Delta h_2}{s_1 \cdot \Delta h_1} \quad . \quad . \quad (15)$$

(γ) *The Drop-weight Method* (*Stalagmometer Method*).—The principle of this method consists in determining the weight of a drop which just falls under its own weight from a circular surface of known radius. At the moment at which it breaks away the force drawing it upwards $= 2r \cdot \pi \cdot \sigma =$ the weight of the drop acting downwards. But since a small quantity of liquid always remains behind on the wetted surface, this method is only available for accurate absolute determinations when special precautions are taken and various corrections are made. For *relative* determinations, on the other hand, it is in general very useful. Instead of determining the weight of one or of a number of the falling drops, it is usual to determine the number of drops into which a measured volume of the liquid divides itself. With two different liquids the weights of equal volumes are in proportion to the densities. If a volume V of one liquid produces Z_1 drops and of another liquid Z_2 drops, then

$$2 \cdot r \cdot \pi \cdot \sigma_1 \cdot Z_1 = V \cdot s_1$$
$$2 \cdot r \cdot \pi \cdot \sigma_2 \cdot Z_2 = V \cdot s_2$$

$$\frac{\sigma_1}{\sigma_2} = \frac{s_1 \cdot Z_2}{s_2 \cdot Z_1}; \quad \sigma_2 = \sigma_1 \frac{s_2 \cdot Z_1}{s_1 \cdot Z_2} \quad . \quad . \quad (16)$$

References :—
S. Sugden. The Parachor and Chemical Valency (1930). Chap. I; XI.
Eucken, Jette, and Lamer. §§ 101-107.

(c) Experimental

The surface tension is determined for $\frac{1}{8}$ and 1 molar aqueous solutions of ethyl, propyl and butyl alcohols, and for a saturated aqueous solution of amyl alcohol, by methods (β) and (γ). The comparison liquid is in each case distilled water.

(1) Capillary Rise Method

Two stout-walled thermometer capillary tubes of different widths are used (diameter between 0·2 and 0·6 mm.) which have millimetre divisions etched along their whole length. Both tubes are very carefully cleaned before use: first with fuming nitric acid or a sulphuric acid-dichromate solution, and then thoroughly washed with distilled water; the liquid to be experimented with is then run through several times. It is not advisable to dry the tubes before beginning the experiment, because even when a dust filter is used impurities always get into the tube when air is sucked through, which makes accurate measurements impossible. The two tubes are placed alongside each other, and tied together by means of a rubber band in such a way that their lower ends are as nearly as possible exactly at the same level. These ends are dipped into the liquid and the difference between the meniscus heights determined from the divisions etched on the tubes. The specific gravity of the liquids is determined by a hydrometer. It is better to work as far away from windows and doors as possible, to avoid strong draughts which produce considerable temperature changes. The results are calculated by means of formula (15). Great care must be taken throughout the experiment to avoid contaminating in any way the liquid under investigation (it must not be touched with the fingers!); even quite small quantities of organic compounds, particularly fats and oils, strongly depress the surface tension, especially that of pure water.[1]

At the end of the experiment the capillaries should be cleaned as described above and kept under distilled water.

(2) Drop-weight Method

A stalagmometer is used, i.e. a pipette with a capillary outflow tube, at the lower end of which a plane surface is ground (Fig. 17).

[1] The longer the carbon chain of the impurity, the more strongly it lowers the surface tension. In a homologous series, for example, at the same molar concentration each successive member lowers the surface tension three times as strongly as the one before. (Traube's Rule.)

The liquid as it flows out wets this surface; a further flow forms a drop, which finally falls off. The dropping must proceed very slowly, in order that the drop may not be prematurely broken off through the kinetic energy of the following liquid. The pipette is marked above and below the bulb, the volume of liquid used in the experiment being thus defined. Since, however, the passage of the meniscus past these marks does not in general coincide with the falling of a drop, the pipette tube is calibrated for a short distance below the upper and above the lower marks. The volume between two such small divisions corresponds to one-tenth of a drop, in the case of water. The particular division, after the upper mark, at which a drop falls for the first time is noted, and the corresponding number of tenths of a drop is added to the total number of drops for the complete volume. This first drop is counted as having the number 0. At the lower mark a similar correction is made: the last drop is taken as the one at the falling of which the meniscus stands nearest (above)

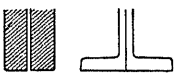

FIG. 17.

the lower mark. Here also the number of tenths of a drop which have still to flow out up to the main mark, is determined by means of the etched divisions. Since the few tenths of a drop which are determined by means of the graduations above and below form only a small correction to the total number of drops (about 200), the difference between the drop size for water and for other liquids may be neglected.

The specific gravities of the liquids are determined with a hydrometer.

The calculation of σ follows from equation (16). Before use the stalagmometer is carefully cleaned with fuming nitric acid or dichromate-sulphuric acid solution, then repeatedly washed out with distilled water and dried. Care must be taken when filling not to leave small air bubbles clinging to the inside of the outflow capillary. For the sake of constancy of temperature the neighbourhood of draughty doors and windows should be avoided.

IV. INTERNAL FRICTION OF LIQUIDS

(a) Theory

(1) LIQUIDS and gases are able to exert force not only *in*, but also *at right angles to*, the direction in which they are streaming. In a flowing liquid forces exist which show that there is "internal friction." Thus, if a surface B is moving past a surface A, and if the intermediate space is filled with liquid, then a force acts upon A in the direction of the movement which can be held in equilibrium by a counterforce, e.g. a spiral spring attached to A. The force K transmitted is larger, the greater the relative velocity v and the surface q of the thin plate which is moved, the smaller the distance d between the plates, and the more viscous the liquid. We have the formula

$$K = \frac{\eta \cdot q \cdot v}{d}, \quad . \quad . \quad . \quad . \quad (17)$$

where η is the viscosity coefficient, or the coefficient of internal friction. η is equal to 1, if with unit distance between the plates and a relative velocity of unity, unit force is exerted upon unit area. The dimensions of η can be seen from (17) to be

$$m \cdot l \cdot t^{-2} = \eta \cdot l^2 \frac{l}{t} \cdot \frac{1}{l}$$

$$\eta = \frac{m}{l \cdot t}.$$

Values of η at 18° are :

Water	0·011	gm. cm.$^{-1}$	sec.$^{-1}$.
Ethyl alcohol . . .	0·012	,,	,,
Methyl alcohol . . .	0·0063	,,	,,
Diethyl ether . . .	0·0024	,,	,,
Glycerine	10·6	,,	,,

(2) The temperature coefficient of η for liquids is negative, i.e. with increasing temperature their viscosity diminishes. For water, for example, it is only half as great at 80° as at 50°. The viscosity of gases, on the other hand, increases strongly with rising temperature, and is independent of the pressure.

At room temperature η for gases is of the order of magnitude of 10^{-4} C.G.S.

(3) In carrying out a measurement in practice, the liquid (or the gas) is allowed to stream through a capillary. At the walls of the capillary a stationary liquid layer adheres, over which the moving liquid slips. The streaming velocity in a capillary increases with the square of the distances from the wall and is greatest at the axis; in the example referred to in the introduction (paragraph 1) the velocity alters linearly with the distance from the surface A (at rest), in the space between this and the moving surface B. According to Poiseuille's law, the volume V of liquid which flows through a capillary in time t is given by

$$V = \frac{p \cdot \pi \cdot r^4 \cdot t}{8 \cdot \eta \cdot l} \quad . \quad . \quad . \quad . \quad (18)$$

p is the constant driving force, l the length, and r the radius of the capillary. By means of this formula η can be determined. In general, relative measurements are sufficient: if equal volumes of two different liquids flow through the same capillary under pressures p_1 and p_2 respectively, then

$$\frac{\eta_1}{\eta_2} = \frac{p_1 \cdot t_1}{p_2 \cdot t_2} \quad . \quad . \quad . \quad . \quad (19)$$

If the weight of the liquid is used as the driving force, then at equal heights of the liquid column the pressures are proportional to the specific gravities s_1 and s_2. Hence

$$\frac{\eta_1}{\eta_2} = \frac{s_1 \cdot t_1}{s_2 \cdot t_2} \quad . \quad . \quad . \quad . \quad (20)$$

(4) Above a certain "critical velocity" the form of the streaming alters, as Reynolds found. Poiseuille's law then no longer holds, and this manifests itself by the fact that the volume of liquid streaming through increases more slowly than in direct proportionality to the pressure. At small velocities the motion of the liquid is "laminary," and in this state all the liquid particles move parallel to one another, so that a coloured thread of liquid introduced into the middle of the capillary does not spread sideways; above the critical velocity, in the so-called "turbulent" state the liquid whirls about irregularly and the coloured substance is immediately distributed throughout the whole of the liquid. The critical velocity U in cm./sec. depends upon the radius r of the capillary,

the viscosity η and the specific gravity s of the liquid, and is expressed formally by:

$$U = \frac{R \cdot \eta}{s \cdot r} \quad . \quad . \quad . \quad . \quad (21)$$

U is calculated from the volume V which flows in time t, and the cross-section of the tube q:

$$U = \frac{V}{t \cdot q}.$$

R is a constant, the so-called "Reynold's number," the value of which has been found empirically to be about 1000. For short capillaries it may fall as low as 500 to 200. It can easily be seen that R is a dimensionless quantity:

$$R = \frac{U \cdot s \cdot r}{\eta} = \frac{V \cdot s \cdot r}{\eta \cdot t \cdot q} = \frac{\text{cm.}^3 \cdot g \cdot \text{cm.} \cdot \text{cm.} \cdot \text{sec}}{\text{sec.} \cdot \text{cm.}^3 \cdot \text{cm.}^2 \cdot g}.$$

For this reason it is always necessary to measure the viscosity at different pressures in order to make certain (through the proportionality of pressure to volume flowing—or, at constant volume, through the constancy of the product of pressure and the time of flow) that one is still within the region of laminary flow. With solutions, which are more viscous than the solvent serving as comparison substance, it is, of course, sufficient that the latter should fulfil the requirement of laminary streaming in the region of pressure in question, since, with the usual supposition that s for the solution is only slightly different from s for the solvent, according to formula (21) a larger value of U must correspond to the larger value of η. If solutions of very different viscosity have to be compared, it is often necessary for the sake of shortening the time of the experiment, to use with the viscous solutions pressures at which the less viscous comparison liquid (usually the pure solvent) would show turbulent streaming. (For example, benzene and concentrated benzene solutions of rubber.) In this case the proper value of the time for comparison is found by extrapolation; for this purpose the constant product pt found in the region of laminary streaming is divided by the high pressure; that is, that value of the time is chosen which would apply to the solvent if it too satisfied the requirement of laminary streaming up to this high pressure.

(5) Certain special viscosity anomalies are often found with colloidal solutions; the viscosity values found with small pressures decrease as the pressure increases, then become constant, and finally appear to increase again as turbulence sets

in. When this happens, only the constant value of the intermediate interval of pressure can be used for comparison. Care should be taken in this connexion with gelatine solutions.

Reference :—
H. Freundlich. Colloid and Capillary Chemistry. English edition, 1925, pp. 539-44.

(b) Experimental

(1) Apparatus

The internal friction of a liquid is determined by measuring the time required for a measured volume of liquid to flow through a capillary tube under a definite pressure (cf. (18)). With the Ostwald viscometer (Fig. 18) the liquid is introduced at *f* and before the measurement is sucked up into the left-hand limb *ab*; the quantity is adjusted so that the upper meniscus is at the mark *c* and the lower at *e*. The time during which the liquid in *k* flows through the capillary *db*, i.e. until the meniscus in the left-hand limb passes the mark *d*, is measured with a stop-watch. The driving force is simply the weight of the liquid in *k*. This force decreases continuously during the course of the experiment and is also different for liquids of different specific gravities.

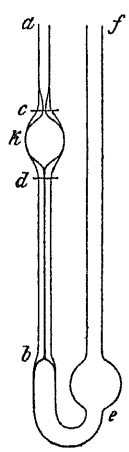

Fig. 18.

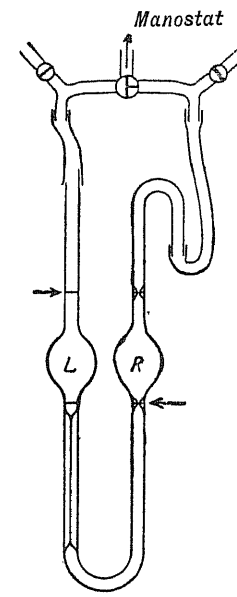

Fig. 19.

With Ubbelohde's viscometer (Fig. 19) which is used for the measurements described below, the inconstancy of the driving force and the influence of differences in specific gravity is eliminated. Before the measurement the liquid fills the space between the two marks indicated on the figure by arrows. By connecting to a manostat (see later) it is forced under constant pressure through the capillary from L to R, so that at the end of the experiment the first meniscus stands at the lower mark

of L, and the other at the upper mark of R. Since the bulbs L and R, which are made as nearly as possible exactly alike, are at the same level, it follows that the hydrostatic pressure of the liquid column in the viscometer acts during the first half of the time of flow in a sense opposite to that in the second half, and therefore on the average the effect is annulled. As a manostat a 5 litre flask with a two-hole rubber stopper serves. The lead to a mercury manometer goes in at one hole, and the vertical limb of a T-piece at the other. The horizontal limb communicates via taps with the atmosphere on one side and with the viscometer on the other. The air is compressed by connecting to a compressed air cylinder, or by means of a bicycle pump. Since the volume of the viscometer bulb L or R is small in comparison with the volume of the manostat, the pressure remains sufficiently constant during the experiment. The time from the beginning of the experiment to the moment when the meniscus on the left passes the lower mark of L is measured by means of a stop-watch to 0·2 seconds. In order to obtain an accuracy of at least 1 per cent. for the time measurement, the duration of the experiment must be at least 20 seconds. Very long times of flow should, however, be avoided, because unless a thermostat is used it is difficult to maintain a constant temperature. For very viscous liquids an apparatus with a wider capillary is used. If the experiment does not last longer than one minute, a sufficiently constant temperature may be obtained by hanging the apparatus in a glass beaker filled with water. With an experiment lasting about 30 seconds and temperature constant to within 0·3° the accuracy of the method is about 2 per cent.

(2) Details of Experimental Procedure

The viscometer is carefully cleaned with dichromate-sulphuric acid solution or fuming nitric acid, dried and filled with the solution to be investigated by a pipette or by suction. With easily volatile solvents suction should be avoided as far as possible. The solution must be dust-free and entirely homogeneous (free from bubbles; otherwise large errors are unavoidable, especially with narrow capillaries). The quantity of liquid is so adjusted by trial that the meniscus levels, when pressure is applied to R, stand exactly at the marks indicated by arrows in the figure. For reversing the pressure the system of taps shown in Fig. 20 is used: A is a three-way, and B and C are ordinary taps. The ends of the U-shaped bent glass tubes

are connected with the two limbs of the viscometer. Before beginning the experiment, B is opened, C closed, A put in position III, and the liquid in L raised until the meniscus on the left is 2 to 3 cm. above the left-hand upper mark, and the meniscus on the right is a corresponding distance below the right-hand lower mark. B is now closed, C opened, and A turned into position II. The liquid is now forced from L into R. The stop-watch is started when the left-hand meniscus passes the upper mark of L, and stopped when it reaches the lower mark of L. By immediately turning A into position I the manostat is cut out and the pressure is equalised in the two limbs, so that no air is blown through the capillary. With volatile solvents the concentration may be considerably altered in this way; also the removal of air bubbles is rather troublesome. (If a small reserve bulb is introduced between the lower mark of the limb L and the beginning of the capillary the danger of bubbling through can be avoided.) In a repetition of the experiment the streaming of the liquid from R to L can be used. In this case the time between passing the lower and upper marks of L is measured.

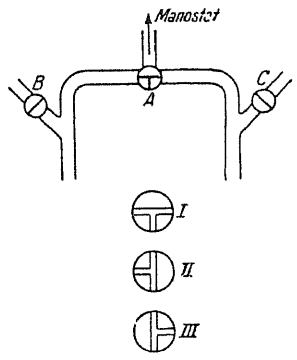

FIG. 20.

The viscometer must remain throughout the experiment in the constant temperature bath (the temperature of which is measured from time to time with a thermometer graduated in $^1/_{10}°$), and must be submerged up to several cm. above the upper marks. The movement of the meniscus can be followed without difficulty through the glass of the beaker and the water. After freshly introducing a liquid, at least ten minutes must be allowed for temperature equilibrium with the bath outside to be established.

Problem: The following gelatine solutions of different p_H are measured at 35°: a 3 per cent. gelatine solution is prepared in warm distilled water, and 10 c.c. portions of the fresh solution are separately diluted with 5 c.c. each of the following liquids:

1. 0·33 N. HCl.
2. 0·10 N. HCl.
3. 0·02 N. HCl.
4. 0·01 N. HCl.
5. 0·001 N. HCl.
6. Distilled water.
7. 0·005 N. NaOH.
8. 0·10 N. NaOH.

As a comparison liquid distilled water is used, also at 35°. With each liquid five measurements at each of three different pressures are made. At any one pressure the times should agree to within 1 per cent. The results are expressed in a diagram: ordinate: pressure; abscissa: time of flow. The points for each solution lie upon a symmetrical hyperbola, provided that the measurements are all in the region of laminary streaming.

In addition the viscosity anomalies in solutions of raw rubber in benzene (0·5 to 1 per cent.) may be investigated. These solutions have to be measured in an apparatus with a wide capillary (1 to 1·5 mm.). As a comparison solution a mixture of equal parts of glycerine and water is used, which at room temperature is about ten times as viscous as water.

V. ADSORPTION FROM SOLUTIONS

(a) Theory

THE boundary between two phases is often characterised by the fact that in its immediate neighbourhood the concentration of substances contained in one of the phases (gas or liquid) is altered, usually increased. This is especially the case if the second phase is a solid with a large surface (animal charcoal, kaolin, colloidal suspensions) and is in contact with gases or solutions. This process of alteration of concentration at a boundary surface is called "Adsorption." It takes place with a definite heat change, called the heat of adsorption.

The quantitative aspect of the adsorption process can often be expressed, within a moderate concentration range, by the Freundlich isotherm.

Expressed in a formula this empirical relationship [1] is

$$\frac{x}{m} = a \cdot c^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad (22)$$

x is the total amount of dissolved substance which is adsorbed by the adsorbent of mass m in equilibrium with a solution of concentration c; a and n are constants for the adsorption process in question and over the range in question, $1/n$ being < 1. Strictly, the adsorbed quantity should be related not to unit mass but to unit surface. For finely divided, or uniform suspensions, however, the surface may be taken as proportional to the total mass. If a graph is plotted with values of c as abscissæ and the corresponding values of $\frac{x}{m}$ as ordinates, then over the whole range of concentration a curve is obtained of the form indicated in Fig. 21. The first part of the curve is linear, because at very small concentrations (as may be proved, in particular, with radio-active substances) there is pro-

[1] The adsorption isotherm of Langmuir (*J. Amer. Chem. Soc.*, **40**, 1369 (1918)), has more theoretical significance.

portionality between $\frac{x}{m}$ and c, i.e. $\frac{1}{n} = 1$. In the region of very high concentrations a limiting value of $\frac{x}{m}$, that is, saturation, is reached. This is the case when the whole of the adsorbing surface is covered with adsorbed substance; $\frac{1}{n}$ is then equal to zero. From each of these two limiting cases there is a gradual transition to the region of moderate concentrations, in which a constant value of $1/n$ can be counted upon.

On taking logarithms in Freundlich's equation, it takes the form

$$\log \frac{x}{m} = \log a + \frac{1}{n} \log c \quad . \quad . \quad . \quad (23)$$

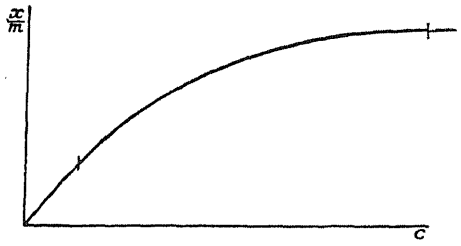

FIG. 21.—Adsorption isotherm.

If, then, the logarithms of $\frac{x}{m}$ are plotted against the corresponding concentrations, a straight line is obtained which intersects the ordinate axis at log a, and has the slope $\frac{1}{n}$.

If the same quantity m of adsorbent is always used, equation (23) may also be written in the form

$$\log x = \log a + \frac{1}{n} \log c + \log m = \log (a \,.\, m) + \frac{1}{n} \log c.$$

If, now, the values of log x as ordinates are plotted against the values of log c as abscissæ, the slope of the resulting straight line is again determined by $\frac{1}{n}$, but the point of intersection of the straight line with the ordinate corresponds to the value of log $(a \,.\, m)$. In this way, from experimentally determined corresponding values of x and c with a given m, the constants a and $\frac{1}{n}$ can be calculated for the adsorption isotherm.

The process of adsorption is reversible. If the concentration of a solution with which a solid body is in equilibrium is lowered —for example, by dilution—then the adsorbed substance is given up until equilibrium under the new concentration is reached in accordance with the adsorption isotherm.

References : see p. 61.

(b) Experimental

(1) Quantitative Determination of the Adsorption of Acetic Acid on Animal Charcoal

By diluting down a 2N acetic acid solution, the following quantities of the dilute acid of approximately the concentrations specified, are placed in six small conical flasks :

No. 1	2	3	4	5	6
150 c.c.	150 c.c.	150 c.c.	125 c.c.	110 c.c.	105 c.c.
0·012N.	0·025N.	0·05N.	0·1N.	0·2N.	0·4N.

The exact content of acetic acid is determined by titration with 0·1N baryta solution and phenolphthalein, pipetting 50 c.c. out of each of the flasks 1, 2, 3, 25 c.c. out of flask 4, 10 c.c. out of 5, and 5 c.c. out of 6, so that in each flask 100 c.c. of liquid remains.

To each flask 3·00 gms. animal charcoal is added, the whole series shaken for ten minutes, and the contents of each flask separately filtered through filter paper ; by pipetting off and titrating, the same quantities as in the original titration, the amounts of acetic acid remaining are determined.

The following data should be recorded in a clear scheme :

1. The initial concentration of acetic acid, expressed in terms of the number of c.c. 0·1N baryta solution which are equivalent to 100 c.c. of the solution ;

2. The final concentration, i.e. the equilibrium concentration of acetic acid after adsorption, expressed in the same way as in 1 ($= c$) ;

3. The quantity of acetic acid adsorbed, equal to the difference between 1 and 2 ($= x$).

In this way corresponding values of x and c are obtained. The results obtained are expressed graphically, taking as abscissæ the equilibrium concentrations c and as ordinates the adsorbed quantities x, on a scale five times greater ; a curve is thus obtained similar to that in Fig. 21 ("adsorption isotherm," or the "simple concentration curve of adsorption").

If the values of log c are plotted in a second diagram as

abscissæ and the values of log x as ordinates, the points obtained lie approximately upon a straight line. The line is so drawn that the distances of the points from the curve is as small as possible. The tangent of the angle of inclination of the straight line to the axis of abscissæ gives the value of $1/n$; the distance from the abscissa axis of the point of intersection with the ordinate axis gives the value of log $(m \cdot a)$.

(2) Reversibility of the Adsorption of Acetic Acid on Animal Charcoal

Into each of four conical flasks 50 c.c. of about 0·05N. acetic acid is put. To Nos. 1 and 2, 50 c.c. of water are added in addition. To each of Nos. 2, 3, and 4, 3·00 gms. of animal charcoal is added, and shaken for about five minutes. To No. 3, after this first shaking a further 50 c.c. of water is added, and shaken for a further five minutes. The contents of flasks 2, 3, and 4 are filtered, and from flask 1 and also from the filtrates of 2 and 3, 50 c.c. is pipetted, and from the filtrate of 4, 25 c.c., and titrated with 0·1N baryta solution and phenolphthalein.

The results are recorded clearly in some such scheme as the following:

	Nos. 1	2	3	4
Initial quantity of 0·05 acetic acid in c.c.	50	50	50	50
Added water in c.c.	50	50	0	0
Added amount of charcoal in *gm.*	0	3	3	3
Further addition of water in c.c.	0	0	50	0
Filtration	—	+	+	+
Quantity pipetted off and titrated	50	50	50	25
C.c. of baryta solution required	—	—	—	—
Amount of acetic acid adsorbed	—	—	—	—

A comparison of the amounts of acetic acid adsorbed in 2 and 4 shows, in agreement with the adsorption isotherm, that in spite of there being equal total quantities of adsorbate, less is adsorbed from the dilute solution than from the concentrated. In 3 the adsorption equilibrium is first established in a concentrated solution; subsequently as much water is added as is required to bring the final concentration to the same value as in 2. The result shows that on dilution, not only does some of the adsorbed acid go back into solution (reversibility of adsorption), but that for the same final concentration the absolute amount of substance adsorbed is the same.

VI. COAGULATION OF A SOL BY ELECTROLYTES OF DIFFERENT VALENCIES

(a) Theory

A COLLOIDAL solution is one in which a definite substance (e.g. gold) is distributed in the form of very small particles (diameter between 10^{-4} and 10^{-7} cm.) as a "disperse phase" in another substance—the "dispersion medium"—e.g. water. This system is also referred to as a "sol" (hydrosol). A distinction is made also between "lyophobe" (hydrophobe), and "lyophile" (hydrophile) colloids. With the first there exists no marked force of "affinity" between the suspended particles and the solvent medium; with the latter, on the other hand, just such affinity forces (formation of solvates or hydrates) are of paramount importance for the formation and stability of the colloidal system. The fact that particles of lyophobic colloids (e.g. of a gold hydrosol) are able to continue freely floating in spite of the action of gravity, although their density often considerably exceeds that of the dispersion medium (for gold $d = 19$) must be referred to the smallness of their dimensions and mass, and the correspondingly large velocity of their thermal motion (Brownian molecular motion). According to the principles of the kinetic theory, at a definite temperature the mean kinetic energy of a single particle, whether of a gas or of a substance dissolved or suspended in a medium is a constant independent of its mass:

$$E = \frac{1}{2} \cdot m \cdot v^2.$$

Hence a small mass involves a large velocity.

The vertical distribution of the particles follows the so-called hypsometric formula. Thus in the atmosphere the concentration of gas particles decreases with height in such a way that the height in which their concentration falls to one-half, is smaller the greater the mass of the particles, the smaller, therefore, their velocity. Analogously, with a sol, if the particles are very small the "half-value" height is large and the colloid in, say, a glass beaker appears to be distributed uniformly. In

the case of very much heavier particles, such as are formed by the coagulation of smaller ones, the half-value height is very small, i.e. the particles all remain practically at the bottom of the beaker. The coagulation of small particles to larger takes place spontaneously, because both the dispersion medium and also the disperse phase tend to decrease their surface, and such a decrease accompanies the formation of larger particles. If as a result the mass of the particles exceeds a certain value, the particles sink to the bottom on account of the small "half-value height," i.e. the colloid "flocculates out."

In a *stable* colloidal solution the spontaneous coagulation of small particles to larger under the influence of surface tension is prevented by the fact that the particles carry on their surface electrical charges of the same sign, so that they repel one another. But by taking up charges of the opposite kind (adsorption of ions) the original charges are neutralised; the mutual repulsion then disappears and the formation of larger particles takes place. This effect can be produced by adding an electrolyte from which ions of the appropriate sign are adsorbed. If the electrolyte is added in such concentration that just sufficient ions are adsorbed to produce the discharge of all the colloidal particles present (these adsorbed ions are, of course, only a fraction of the total quantity of ions present), then the precipitation is complete and the liquid above the precipitate is perfectly clear. If the electrolyte concentration is too small for this the colloid is only partially discharged and the supernatant solution remains more or less cloudy. Frequently, however, the solution remains cloudy, when the concentration of added electrolyte exceeds what would be sufficient for complete precipitation; this is because under some circumstances an amount of the ions is adsorbed which exceeds what is necessary to discharge the colloid, so that the colloid now receives a charge opposite to that which it had originally, and is thus stabilised. (*Re-charging* and *peptisation* of the colloid.)

In the following problem the recognition of the neutral point by means of the optimum clarification is applied to determine the precipitation concentrations of ions of different valencies, which are then related to the Freundlich adsorption isotherm.

Suppose that with a given colloidal solution—say the negatively charged As_2S_3 sol.—complete flocculation of a definite amount, e.g. 10 c.c. in each case, is produced first by univalent ions, then by divalent, and in a third experiment by trivalent ions ($Na^{\bullet}$; $Ba^{\bullet\bullet}$; $Al^{\bullet\bullet\bullet}$). Then for neutralisation of the original negative charge the amount of $Ba^{\bullet\bullet}$ ions which must be adsorbed

is only half as great (expressed in mols (gram-ions) as the amount of $Na^{\cdot}$ ions, and the amount of $Al^{\cdot\cdot\cdot}$ ions is only one-third. The adsorbed molar quantities of $Na^{\cdot}$, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ are therefore in the ratio of $1 : \frac{1}{2} : \frac{1}{3}$. That is

$$\frac{x_1}{m} = \frac{x_2 \cdot 2}{m} = \frac{x_3 \cdot 3}{m} = \frac{x_\nu \cdot \nu}{m} = \text{constant},$$

or

$$\frac{x_\nu}{m} = \frac{\text{constant}}{\nu},$$

where the index of x is the charge ν of the adsorbed ion. If the assumption is made that in the adsorption isotherms of these three cations both a and n have the same value, then the further relationship must hold :

$$\log \frac{\text{constant}}{\nu} = \frac{1}{n} \log c + \log a \quad . \quad . \quad (24)$$

or

$$\log \nu = -\frac{1}{u} \log c + (\log \text{constant} + \log a)\ ^{1} \quad . \quad (25)$$

If the assumptions made are valid, it would be expected that on plotting the logarithm of the valency (formula 25) or the logarithm of the reciprocal of the valency (formula 24) against the corresponding molar precipitation concentration, a straight line would be obtained. This is in fact found to be the case.

References :—
Eucken, Jette, and Lamer. §§ 153 ; 167 ; 172.
Nernst, Bk. II, Chap. XIII ; Bk. III, Chap. III, pp. 578-80.
H. Freundlich. The Elements of Colloid Behaviour, English edition, 1925.
H. S. Taylor. Chap. XX.

(b) Experimental

(1) Preparation of a Colloidal A_2S_3S-Solution

Five grams As_2O_3 are boiled for ten minutes with 200 c.c. of distilled water. The solution is cooled to room temperature, filtered from excess As_2O_3, and diluted to 1000 c.c. A rapid current of H_2S is passed through until the solution, at first opalescent, begins to grow cloudy. Excess H_2S is removed by bubbling CO_2 through for ten minutes. The solution is then filtered.

[1] Strictly speaking c refers to the concentration of the ion in question in the solution above the precipitated colloid. But since the quantity of ions adsorbed is usually very small, this concentration can be put equal to the concentration calculated from the volume of the colloidal solution and the amount and concentration of the added electrolyte solution.

(2) The Precipitation

Into each of ten test-tubes 10 c.c. of the sol is measured. Before use the tubes are carefully cleaned, steamed out for a few minutes and repeatedly washed out with distilled water. From a burette 0·5 c.c. of $m/500$ $BaCl_2$ solution is added to the sol in the first tube, which is then closed by a rubber stopper, gently inverted twice without shaking, to cause thorough mixing, and placed in the test-tube rack. To the second test-tube 1 c.c. of the $BaCl_2$ solution is added; it is then closed with a rubber stopper, treated as the first, and placed beside it in the rack. The remaining eight tubes are treated in the same way *quickly* one after the other, adding 1·5; 2; 2·5 up to 5 c.c. of the $BaCl_2$ solution. After waiting fifteen minutes after the last tube, the whole series is inverted again; after a further five minutes the tubes are compared in a light falling directly upon them, and in front of a dark background, in respect of the degree of clearing of the supernatant solution. The lowest concentration at which the supernatant solution looks quite clear is the precipitation concentration. This precipitation concentration can be determined more exactly by making small additions from a suitable pipette, in steps of 0·1 c.c. of electrolyte solution.

If, however, the solution is not entirely clear at any one of the concentrations, but instead the turbidity increases from tube 1 to 10, this is an indication that even the first addition of 0·5 c.c. produced too great a concentration of electrolyte, and the excess of ions adsorbed caused a re-charging of the colloid. The experiment must then be repeated with smaller additions (0·05 to 0·5 c.c.).

If, on the other hand, there is a gradual decrease of the cloudiness, without even the last tube being quite clear, then the amount of electrolyte added is too small. In the repetition a more concentrated $BaCl_2$ solution must be used.

It is important always to keep the experimental conditions exactly as they have been described. With the more closely graded additions, at least ten minutes must be allowed after the second mixing, before making the comparison, because here the differences in the rates of sedimentation become apparent more slowly. All to-and-fro movement of the rack of tubes is to be avoided.

A second experiment is made in exactly the same way with $m/2500$ potassium alum solution and a third with $m/5$ NaCl solution. (With the alum it is only the precipitating action

of the $Al^{\cdot\cdot\cdot}$ which is of any importance.) With alum the point of optimum clearness is usually very easy to recognise, because when the precipitation concentration is overstepped even slightly re-charging and peptisation of the colloid is caused. With NaCl the point is less sharply defined. Usually the solution above the precipitated colloid appears clear when a definite addition of electrolyte has been made, and cloudiness appears again only after a considerable further addition (several cubic centimetres) has been made. In other words, with univalent electrolytes a considerable increase of ionic concentration is necessary for re-charging and peptisation of the precipitated sol. As the precipitation concentration is taken the *lowest* concentration at which complete clarification is produced.

(3) Calculation of the Precipitation Concentration

Supposing that 3·5 c.c. of an $m/500$ $BaCl_2$ solution is required for the precipitation of 10 c.c. of the sol., the precipitation concentration is $\frac{3 \cdot 5}{500 \cdot 13 \cdot 5}$ mol/litre. The number 13·5 takes account of the fact that the volume after addition of the electrolyte amounts to 13·5 c.c.

(4) Representation of the Results on a Graph

Since the ionic quantities absorbed when the original charge is completely neutralised are as $1 : \frac{1}{2} : \frac{1}{3}$, the logarithms of 1, $\frac{1}{2}$, and $\frac{1}{3}$, i.e. 0, $-\log 2$ and $-\log 3$ are plotted on the ordinate axis. The logarithms of the precipitation concentrations are on the abscissæ axis. Thus if c is 0·001805 mol/litre, the logarithm is $0 \cdot 256 - 3 = -2 \cdot 744$. For graphical representation of data on logarithmic paper, see page 113.

VII. DETERMINATION OF HYDROGEN ION CONCENTRATION BY MEANS OF INDICATORS

(a) Theory

(1) The Importance of $H^{\cdot}$-concentration

For many chemical processes it is not the *total amount of acid*, given by the normality of the acid and which is determined by titration, which is of importance, but rather the concentration of *free hydrogen ions*, which is connected with the total acid concentration by the apparent degree of dissociation (see p. 16). This determines, for example, the velocity of many reactions and the behaviour of colloids. It is only necessary to recall the numerous hydrolytic processes which take place either directly under the action of acids, as for example the hydrolysis of esters or the inversion of cane sugar, or in the presence of enzymes the activity of which is influenced by acids, e.g. the degradation of white of egg by pepsin, the breakdown of starch by diastase or the splitting up of cane sugar by invertase. Also the decomposition of H_2O_2 proceeds at a rate which varies with the strength of the acid reaction.

(2) Symbols and Method of Calculation

Following the suggestion of P. Sörensen, as a symbol to express hydrogen ion concentration, the *negative* of the decimal logarithm of $H^{\cdot}$-concentration is used, and is called p_H. A solution with a hydrogen ion concentration of 10^{-1} is accordingly expressed by $p_H = 1$, and with $H^{\cdot}$-concentration 10^{-3}, by $p_H = 3$. If the $H^{\cdot}$-concentration is 1 mol/litre, then $p_H = 0$; at 10 mol/litre $p_H = -1$. Thus the larger the p_H, the smaller is the $H^{\cdot}$-concentration. p_H may also be defined as the volume in litres in which 1 mol of $H^{\cdot}$ is contained. The p_H is particularly convenient for graphical representation of any quantity which depends upon $H^{\cdot}$-concentration.

The translation of $H^{\cdot}$-concentration into p_H is as follows: the logarithm of the number in question is taken (the number

is expressed as a power of 10) and the logarithm is multiplied by -1. For example, if the $H^{\cdot}$-concentration of an $\frac{n}{10}$ HCl solution is ·091, i.e. $9{\cdot}1 \times 10^{-2}$, then the logarithm is $0{\cdot}96 - 2 = -1{\cdot}04$. $c = 10^{-1{\cdot}04}$ and therefore corresponds to a $p_H = 1{\cdot}04$. Conversely, p_H is calculated in terms of $H^{\cdot}$-concentration by multiplication by -1 and taking the antilog.: given that $p_H = 4{\cdot}70$. The $H^{\cdot}$-concentration is therefore $10^{-4{\cdot}70}$. Now $-4{\cdot}70 = 0{\cdot}30 - 5$; the antilog. of 0·30 is 2·0. Thus $p_H = 4{\cdot}70$ corresponds to an $H^{\cdot}$-concentration of $2{\cdot}0 \,.\, 10^{-5}$. A decrease of 0·3 in p_H means that the $H^{\cdot}$-concentration is doubled. A solution of $p_H = 4{\cdot}70$ has twice as great an $H^{\cdot}$-concentration as a solution of $p_H = 5{\cdot}0$.

What has already been said applies analogously to alkaline solutions also. The apparent degree of dissociation of a 0·1 normal NaOH solution amounts, say, to 0·84. Its OH'-concentration is therefore 0·084 or $8{\cdot}4 \times 10^{-2}$. From this is calculated in the same way as before $p_{OH} = 1{\cdot}08$. The less convenient quantity p_{OH} can be calculated to p_H without difficulty by taking into consideration that the ionic product of water (see p. 204) at 18° has the value $10^{-14{\cdot}14}$.

$$C_{H^{\cdot}} \,.\, C_{OH'} = 10^{-14{\cdot}14}$$
$$\log C_{H^{\cdot}} + \log C_{OH'} = -14{\cdot}14$$
$$p_H + p_{OH} = 14{\cdot}14.$$

Hence a p_{OH} of 1·08 corresponds to a p_H of $14{\cdot}14 - 1{\cdot}08 = 13{\cdot}06$. Pure water contains $H^{\cdot}$ and OH' in equal concentration, actually, a concentration of $\sqrt{10^{-14{\cdot}14}} = 10^{-7{\cdot}07}$. True neutrality therefore lies at $p_H = 7{\cdot}07$. All solutions with a p_H smaller than 7·07 are therefore acid, all with a greater p_H are alkaline.

(3) General Remarks on the Determination of $H^{\cdot}$-concentration

The determination cannot be made by *titration*, which measures only the total quantity of acid in the solution; in the titration in proportion as $H^{\cdot}$ forms undissociated water with the OH' of the alkali, fresh acid continually dissociates until the whole of the acid present has been neutralised.

In the first place, certain reactions, of which the velocity is proportional to the $H^{\cdot}$ concentration, are applicable. Among the methods which may be used are:

1. The hydrolysis of diazoacetic ester, in which nitrogen is split off.

2. The hydrolysis of methyl acetate to methyl alcohol and acetic acid (see p. 117).

3. The inversion of cane-sugar (see p. 114).

4. The splitting of diacetone alcohol into two molecules of acetone, which proceeds at a rate proportional to the OH' concentration, and so inversely proportional to that of $H^{\cdot}$.

All these methods are only of use with comparatively large $H^{\cdot}$- or OH'-concentrations, since otherwise the reactions in question proceed too slowly. Some of them are also very sensitive to the presence of certain neutral salts and kinds of ions, which cause disturbing side reactions.

Besides these, two electrical methods are of importance:

5. The determination of the potential of a hydrogen electrode, which depends upon the $H^{\cdot}$-concentration (see p. 202), can be used in nearly all cases and is very accurate.

6. With pure acids the degree of dissociation, and with it the $H^{\cdot}$-concentration, can be determined from $\frac{\Lambda_v}{\Lambda_\infty}$ by means of conductivity measurements (see p. 155).

7. Finally the colorimetric method described immediately below can often be employed with success, and it does not necessitate any special apparatus as in methods 5 and 6.

(4) The Colorimetric Indicator Method

The method depends upon the fact that the change of colour of different indicators takes place at various $H^{\cdot}$-concentrations. According to W. Ostwald, indicators are to be regarded as weak acids or bases with which the undissociated molecule shows a different colour from the coloured anion or cation formed by dissociation. [According to more recent views the change in colour on formation of an undissociated molecule, say of an acid, from the ions may be looked upon as a result of the deformation of the electronic system of the anion under the influence of the $H^{\cdot}$ nucleus taken up. In many cases (Hantzsch) a shifting of the atoms or bonds within the molecule takes place as a result of the adding on of the $H^{\cdot}$, and the colour change is then referred to differences of constitution between anion and acid (e.g. benzenoid and quinonoid forms).] An indicator acid is therefore only very slightly dissociated when the $H^{\cdot}$-concentration is large, in accordance with the equilibrium

$$\frac{H^{\bullet} . A'}{HA} = \text{constant.}$$

By the mass action equilibrium, in the presence of a large quantity of $H^{\bullet}$, only a very small quantity of the coloured anion A' is stable, i.e. the indicator or the solution containing it shows the colour of the undissociated molecules. In alkaline solution, on the other hand, that is with very small $H^{\bullet}$-concentration, practically all the molecules are dissociated, and the solution has the colour of the indicator anions. Between these two extremes is a transition region, where the undissociated molecules and the colour anions are present in amounts of the same order of magnitude. The solution then shows an intermediate colour varying between the colours of the strongly acid and strongly alkaline solutions, depending upon the relative amounts of the two coloured constituents (see p. 70).

The turning-point, or more accurately the transition from the "acid" to the "alkaline" colour occurs with different indicators at quite different $H^{\bullet}$-concentrations and over different ranges of concentration. These data have been accurately determined by Sörensen and his co-workers for a large number of indicators, in a series of systematic investigations. If now samples of a solution of unknown $H^{\bullet}$-concentration are tested separately with different indicators having known and systematically spaced-out transition regions, then one of the indicators will find itself just in its transition region, and will show its transition colour. Thus the unknown $H^{\bullet}$-concentration is determined to a first approximation, since it is confined within two limiting values, namely, the turning-points of this indicator.

The method may be refined by preparing several intermediate steps of $H^{\bullet}$-concentration within the transition region found, by means of special comparison solutions; the indicator in question is added and the comparison solution in which the shade of transition colour of the indicator agrees most closely with the solution of unknown $H^{\bullet}$-concentration is noted.

Such accurately known and closely stepped intermediate $H^{\bullet}$-concentrations, and especially also very small $H^{\bullet}$-concentrations, which would, for example, be rapidly altered by carbonic acid from the atmosphere, can be prepared conveniently and exactly with the help of "buffer solutions," which are obtained by mixing together certain standard solutions. For this purpose, according to Sörensen's instructions mixtures of glycocoll with hydrochloric acid or sodium hydroxide, or of secondary sodium citrate with hydrochloric acid or sodium hydroxide, or of

primary and secondary alkali phosphates, or of sodium hydroxide and "borate" are used.[1]

Their $H^{\cdot}$-concentrations have been accurately determined with the hydrogen electrode. The results are expressed graphically on curves [2] which may be used for reference: the ordinates give the composition, the abscissæ the p_H of the different mixtures. The total amount of liquid is always taken as 10 c.c. Ordinate 0 corresponds to pure 0·1N HCl, or NaOH, or primary potassium phosphate; the ordinate 10 to pure glycocoll, or secondary sodium citrate, or secondary sodium phosphate or "borate." The way in which the curves are read will be understood from the following examples:

The p_H obtained from the following mixtures are:

5·2 c.c. glycocoll + 4·8 c.c. HCl	p_H = 2·00
5·6 c.c. citrate + 4·4 c.c. HCl	p_H = 4·00
1·2 c.c. sec. phosphate + 8·8 c.c. prim. phosphate .	p_H = 6·00
6·0 c.c. borate + 4·0 c.c. NaOH	p_H = 10·00

The name "buffer solutions" arises from the peculiarity of these solutions, that they change their $H^{\cdot}$-concentration only within narrow limits when even strong acids are added in quantities that are not too large. The reason for this behaviour is that the "buffer" is able, to a considerable extent, to "bind" the additions of this kind by salt formation. With glycocoll $(NH_2)CH_2COOH$, for example, the NH_2-group reacts with acids and the COOH-group with bases; secondary sodium citrate is converted by acids into primary, and by alkalies into tertiary citrate; in a mixture of primary and secondary phosphate acids shift the composition in favour of the primary, and bases in favour of the secondary salt; the so-called "borate" is an alkali boric acid solution, a mixture of boric acid and primary borate in the ratio of 1 : 1; addition of acid causes change of borate into boric acid, and of alkali the reverse reaction. The buffer action, of course, only persists as

[1] Hydrochloric acid: N/10;
[illegible]: N/10;
[illegible]: 7·505 gm. glycocoll and 5·85 gm. NaCl in 1 l. water;
Primary phosphate: 9·078 gm. KH_2PO_4 in 1 l. water;
Secondary phosphate: 11·876 gm. $Na_2HPO_4 . 2H_2O$ in 1 l. water;
Citrate: 21·008 gm. crystalline citric acid dissolved in 200 c.c. N NaOH, and diluted to 1 l.;
Borate: 12·404 gm. boric acid dissolved in 100 c.c. N. NaOH and diluted to 1 l.
For the preparation of the solution carbon dioxide—free, boiled-out water is used.
See *Bioch. Zeitschrift*, **21**, (1909), p. 131 *seq.*; Standard solutions, p. 167.
[2] Obtainable from Julius Springer, Publishers, Berlin.

must lie between these two groups. Thus it is clear that a red or orange colour with thymol blue shows at once that the p_H lies below 2·8, and the testing with other indicators, which must all show the "acid" colour, becomes superfluous. Conversely, the red "alkaline" colour with cresol red is only compatible with the alkaline colour for all the preceding indicators. Sometimes by careful consideration and closer reference to the table it is possible, even in this preliminary experiment, to locate the unknown p_H quite closely. For example, if phenol red shows its transition colour (6·8-8·4), but bromthymol blue is deep blue (p_H 7·6), then the range remaining to be investigated is only 7·6-8·4. If at the same time thymol blue is still yellow, then the range is narrowed to 8·0-8·4.

For the further investigation is chosen the indicator for which the unknown $H^{\bullet}$-concentration lies approximately in the middle of the transition range, as nearly as can be estimated from (2).

3. To 10 c.c. of liquid to be tested the indicator selected is added by drops until the solution has a moderately strong colour.

4. Buffer solutions are now prepared in 10 c.c. portions of closely graded $H^{\bullet}$-concentration, covering the transition region of the indicator in question—or, if the limits have already been fixed more closely, then over this narrower range—by mixing together appropriate quantities of two standard solutions, chosen by reference to the table of curves, in such a way that the range is divided into steps of 0·2 p_H. It is important to use only solutions for which the curves at the $H^{\bullet}$-concentration in question are *steep*, so that a small accidental error in the composition of the solution causes only a small error in the p_H.[1]

Thus for the range p_H 3·8 to 5·0 mixtures of citrate + HCl should be chosen, not glycocoll + HCl; or for p_H 6·6 to 7·6 mixtures of primary and secondary phosphate, not of citrate + sodium hydroxide; or for p_H 7·8 to 8·2 borate + HCl, not glycocoll + sodium hydroxide.

To each of the comparison solutions the same number of drops of the indicator used are added as in (3), so that there are now a number of transition colours in the region which is of interest. The tubes are again arranged in the test-tube rack in order of increasing p_H, and there is then no difficulty, with the aid of a white background, in putting the tube with the unknown $H^{\bullet}$-concentration in its right place in the series. If the tubes are now put over a white ground and looked into from above,

[1] The mixtures to be avoided are denoted by dotted parts of the curves obtainable from Julius Springer (see p. 68).

small differences can still be easily seen. After the limits have been narrowed down to within 0·2 p_H in this way, three more intermediate steps with intervals of 0·05 p_H are mixed, and after adding the same number of drops of indicator as before, compared with the unknown solution. The value can be found without difficulty to $\pm$ ·05 p_H.

It is essential always to prepare a sufficient number of intermediate steps so that the unknown solution can be arranged in order *within the series* and not merely *at one end* of the series, where an accurate comparison of the colour is very difficult. If this is not possible with the indicator which is being used, the adjacent indicator in the sequence of transition regions must be used.

(2) Coloured Solutions.

For strongly coloured solutions the method is useless. But if there is only a faint coloration before the indicator is added, then the comparison buffer solution is given the same shade of colour by addition of a suitable colouring matter. For this purpose one of the indicators mentioned above can sometimes be used, provided that in the preliminary experiment (2) it has been found that the $H^{\cdot}$-concentration in question lies far away from the transition region of the indicator to be used, so that it shows a purely alkaline or purely acid colour. The intensity of the colour is regulated by addition of more or less of the indicator.

(3) Cloudy Solutions

When cloudy solutions are being used, e.g. in the investigation of colloidal albuminous substances or suspended colonies of bacteria, the comparison solutions must be as far as possible brought to the same degree of cloudiness. For this purpose only reagents with an exactly neutral reaction can be used, such as a fine silica suspension, or colloidal barium sulphate, but not aluminium or zinc hydroxides. Such alkaline or acid reacting substances would alter the $H^{\cdot}$-concentration of the solution, at any rate slightly, so that the data obtained from the table of curves could not be relied upon.

Determination with cloudy or weakly coloured solutions can be done without any addition to the solutions, with the aid of the Walpole comparator, which depends upon the additivity of cloudiness and of colour when separated in two tubes lying one behind the other. On looking through such a pair of tubes

the impression is the same as on looking through a cloudy and coloured solution.

Three pairs of equally wide test-tubes are arranged in a rack in front of a white background, in such a way that one of the two tubes of a pair is behind the other. 10 c.c. of the cloudy solution under investigation is added to each of the three tubes at the back, and to the middle one in addition as many drops of the indicator selected as are required to produce a clearly recognisable colour in the transition region. In the front tube of the middle pair 10 c.c. of distilled water is placed, and in the two side tubes 10 c.c. of suitable buffer solution plus the same quantity of indicator as in the unknown solution. The composition of these buffer mixtures is then varied until the appearance of the middle pair of tubes (cloudy solution coloured by the indicator + water) is as far as possible the same as that of one of the side pairs (cloudy solution + buffer solution coloured by indicator) or lies in between the shades of colour of the two sides.

The comparator can be used in a similar way for weakly coloured solutions.

VIII. CALORIMETRY

(a) Theory

(1) *General.*—When two states of matter can be interchanged by introduction or removal of energy, then by the first law of thermodynamics this *energy difference* ΔU is constant and independent of the way in which the energy change is brought about. Usually one part of ΔU is transformable into *work* (w) and another part appears in the form of *heat* (q). In general, therefore, $\Delta U = q - w$. (Energy transferred to the system, and therefore withdrawn from the surroundings, is reckoned as $+$; energy given up by the system, and passing into the surroundings, as $-$.) How much of ΔU is in the form of work and how much in the form of heat absorbed or given out, depends not only upon the initial and final state but also upon the way in which the process is carried out. In the calorimetric determination of ΔU the arrangement is made as far as possible such that no work is done, but that only heat appears: $w = 0$; $\Delta U = q$. In the processes discussed in this chapter, the dissolving of a salt in water and the neutralisation of an acid by a base, both under atmospheric pressure, the work is equal simply to the change in volume of the system multiplied by the atmospheric pressure. In the neutralisation of a dilute acid by a dilute alkali this change of volume is always very small. It amounts, for example, on mixing together 200 c.c. of 0·25N HCl and 200 c.c. of 0·25N NaOH to $-$ 0·9 c.c. ($w = +$ 0·0009 L. Atm. = 0·021 cal.;[1] $q = -$ 685 cals.). Also, in the dissolving of a salt, the difference in volume between salt + water on the one hand and the solution which is formed on the other is usually very small. E.g. in the dissolving of 10 gms. KCl (= 5 c.c.) in 400 gms. water, as in the calibration of the calorimeter, it is $-$ 1·5 c.c. The work in this case is 0·0015 L. Atm. = 0·036 cal., while the heat of reaction q at 25° amounts to

[1] 15° cal. = the quantity of heat which warms 1 gm. of water from 14·5° to 15·5°.

+ 568 cals. In both the experiments done w may be put = 0 and hence $\Delta U = q$.

(2) For many salts, ΔU is positive; in the process of solution heat is used up. If the reaction takes place in a calorimeter vessel isolated from the surroundings, this heat cannot be drawn from the surroundings, but is provided entirely from the heat content of the system itself: in other words, the system cools. Conversely, for the same reason the heat of neutralisation developed when $H^{\cdot}$ and OH' combine to undissociated water cannot be given up to the surroundings, so that the heat content of the system is increased, and it becomes warmer. The calculation of the heat of reaction is made in both cases by multiplying the temperature difference by the "heat capacity" of the system. By heat capacity is meant the quantity of heat which produces a temperature change in the system of 1°. Since during the reaction heat exchange with the surroundings does take place to a small extent, this factor also has to be taken into account in the calculation. It is noticed as the so-called "drift," i.e. as a spontaneous gradual change in temperature of the system, which is larger the greater the temperature difference and the worse the insulation, between calorimeter and surroundings. With intensive stirring the heat of stirring developed can also contribute to the "drift." It is simplest to take account of it by a graphical method, as explained later.

(3) The heat of solution of a salt, referred to 1 gm. or to 1 mol, depends upon whether the salt is dissolved in pure solvent or in a solution. With the former, the relative quantities of salt and solvent, with the latter the initial and final concentrations of the solution, are important. For the three following more important cases, special names are used: if the solution takes place into a very large volume of pure solvent, so that an ideal dilute solution is formed, the heat of reaction is referred to as the "first heat of solution." If for the solution process just as much solvent is used as is needed to produce a saturated solution, the accompanying heat effect is called the "total heat of solution." When the salt is dissolved in an almost saturated solution, the "last heat of solution" is spoken of. This last reaction heat is important for the temperature and pressure coefficients of solubility. With many salts these different heats of solution have different signs. An increase or decrease of solubility with rise of temperature is found, respectively, with negative or positive last heat of solution.

Heats of solution also depend upon the temperature at

which the reaction takes place. The relationship is expressed by Kirchoff's law: $\frac{d(\Delta U)}{dT} = c_v' - c_v$. c_v is the sum of the heat capacities in the mixture of salt and solvent considered, c_v' that of the solution formed.

(4) The heat of neutralisation, which is set free when a dilute solution of a strong acid is mixed with a dilute solution of a strong base has, as is well known, the same value of 13·7 k. cals. at 20° (calculated for 1 gm. equivalent of $H^{\cdot}$ and OH') for different acids and bases. This is explained by the fact that the two initial solutions are practically completely dissociated; the heat of neutralisation is thus simply the heat of reaction of free $H^{\cdot}$ and OH' to undissociated water. With weak acids and weak bases, which even in dilute solution are only partially dissociated, there is added to the neutralisation heat the heat of dissociation of the dissolved molecules into the corresponding ions, and this may be either negative or positive. Accordingly the heat of neutralisation is smaller or larger than 13·7 k. cals.

References :—
Eucken, Jette, and Lamer. §§ 199-202.
Nernst. Bk. III, Chap. IV, p. 597; Bk. IV, Chap. I.
H. S. Taylor. Chap. VI.

(b) Experimental

(1) The Calorimeter. (Form designed by White.)

(α) *The Apparatus.*—As reaction vessel an ordinary wide-mouthed thermos-flask of about 600 c.c. capacity is used. In order to make the heat exchange with the surroundings as uniform as possible, it is placed in a large water-container so that the rim of the Dewar vessel projects about 2 cm. above the water level. The temperature of this large quantity of water alters only very slightly during the time of an experiment. Further, in order to avoid as far as is practicable the effects of heat radiation and irregular air-currents from above into the calorimeter, a hollow double cover, of 1 mm. thick copper sheet (Fig. 22) is added; this extends so far below the rim of the calorimeter that it dips into the outer water-bath to a depth of several cm. Because of the good conductivity of copper, it quickly takes the temperature of the water. With this arrangement of apparatus the liquid in the calorimeter is surrounded on all sides by a space at a uniform and almost constant temperature; the drift is therefore very regular and, because of the good insulation, very slight. The cover has three

openings, the two smaller for the stirrer and the thermometer, and the larger for introducing the salt. For the stirrer a glass rod is used, the lower part of which is bent round into a ring of suitable size. With Dewar vessels having a strongly concave end, an upright, flat ring is better; the lower part of this is made to fit the curvature of the bottom of the Dewar as well as possible, and the stirrer is rotated round the shaft as a vertical axis. Temperature is measured by a thermometer graduated in $^1/_{50}°$. The salt is contained in a thin-walled test-tube, which before the measurement is held by a bored cork in the large opening in the cover. The lower end must dip sufficiently deeply into the calorimeter water for temperature equalisation between salt and solvent.

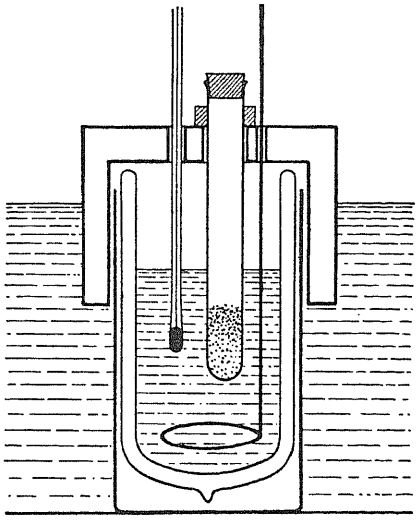

FIG. 22.

The heat capacity of that part of the system which takes part in the temperature change is most simply determined by the aid of an exactly known heat of reaction. Heat capacity $= \frac{\text{Heat of reaction}}{\text{Temperature change}}$. (Where accurate electrical measuring instruments are available, another convenient method of calibration is the introduction of a known amount of electrical energy.) For the method of calibration described here, the heat of solution of 10·00 gms. of analytically pure KCl in 400 c.c. of distilled water, is used. At 19·71° this amounts to 617 cals. and at 25·00° to 568 cals.: since the specific heats of water and of dilute KCl solution alter only slightly, and in the same sense, over this temperature range, the temperature coefficient of this heat of reaction (see p. 76) may be taken as constant over the range in question, and for intermediate temperatures the heat of solution may be interpolated linearly. As reaction temperature is taken the mean temperature of the experiment, i.e. the arithmetic mean of the initial and final temperatures of the reaction, arrived at by taking into account the correction for drift, as explained below.

(β) *Experimental Procedure.* (1) *Determination of the Heat Capacity.*—The analytically pure KCl is ground up and 10·00 gms. weighed into the selected test-tube on an analytical balance. On a rough balance 400·0 gms. distilled water is weighed into the Dewar vessel, with an accuracy of 0·2 gm. The temperature of the water should be between 20° and 25°. The stirrer is put in place, the metal cover fitted over and the vessel sunk into the outer water-bath. The temperature of the water-bath should not differ from that of the calorimeter liquid by more than 2° or 3°. The thermometer fastened in its cork is put through the proper opening in the cover to such a depth in the calorimeter vessel that the thermometer bulb is approximately in the middle of the water. The opening of the test-tube containing the KCl is closed with a cork, and at about 1 cm. below the rim a wide bored cork is fastened, by means of which it can be handled conveniently and without loss of heat; the position of the cork is so chosen that the lower part of the tube, up as far as it is filled with the salt, dips into the calorimeter liquid. In order that the minimum possible amount of calorimeter liquid may remain hanging on the tube when it is removed, the thinnest possible layer of vaseline is put on it. After waiting about ten minutes after first putting the apparatus together so that the salt and the water may reach the same temperature, stirring is begun, as regularly as possible and not too strongly. *Care should be taken not to strike the thermometer bulb.* At half-minute intervals the thermometer is read with a lens and recorded. Immediately before the reading the thermometer is tapped with an empty thermometer case at the place where it is to be read. The spontaneous change of temperature per minute, determined in this way—the drift—is negative or positive according to whether the temperature of the calorimeter liquid is higher or lower than that of the outer bath. If the drift has been constant for ten minutes, then, whilst continuing the same regular stirring, the salt is quickly dropped in: the test-tube is held by the cork, withdrawn from the calorimeter and the contents emptied in through the opening into the calorimeter water. By working quickly the possible heat interchange between the salt and the atmosphere during this operation is made practically negligible. (0·1° temperature difference between salt and water, with the 10 gms. used, would introduce an error of 0·17 cal. = ca. $^1/_{3600}$ of the heat of reaction. For solid KCl $c = \frac{\text{Mol. heat}}{\text{Mol. wt.}} = \frac{2{\cdot}62}{74{\cdot}56} = 0{\cdot}166$ cal.) The opening is then closed by a cork. The dissolution of the salt takes

place rapidly with vigorous stirring, and is over in from one to two minutes. One minute after introducing the salt the temperature is again read every half-minute. This is continued until the drift is again uniform for ten minutes.

For calculating the heat capacity, the temperature readings are plotted on mm. paper as ordinates, and the absolute time as abscissæ, on a fairly large scale. On joining up the points, the drift before and after the measurement takes the form of gently sloping straight lines (Fig. 23). Since a spontaneous heat interchange between calorimeter and surroundings has taken place during the reaction, a correction must be applied to the direct reading of the temperature lowering caused by the reaction. This is most simply done (and with sufficient accuracy for the apparatus employed) by extrapolating on the time-temperature diagram the drift before and after the reaction, up to the point on the time axis when the salt was dropped in. The temperature difference found in this way corresponds to the heat of reaction which would have been observed if the reaction had taken place completely at the moment of dropping in the salt, and up to this moment and immediately afterwards there had been a regular drift. The arithmetic mean of the initial and final temperatures found in this way is taken, and from the data on page 77 the magnitude of the heat of reaction for this temperature is calculated. Division of this heat of reaction by the corrected temperature difference gives the heat capacity of the system when it contains 403·5 c.c. of solution (see p. 74). Subtracting the heat capacity of the solution, which on account of the great dilution may be taken as identical with the heat capacity of the water contained in it, there is left the heat capacity of the Dewar vessel, the thermometer and stirrer, in so far as they take part in the temperature changes, with this amount of liquid in the vessel. When there is either more or less liquid, this heat capacity is, of course, different.

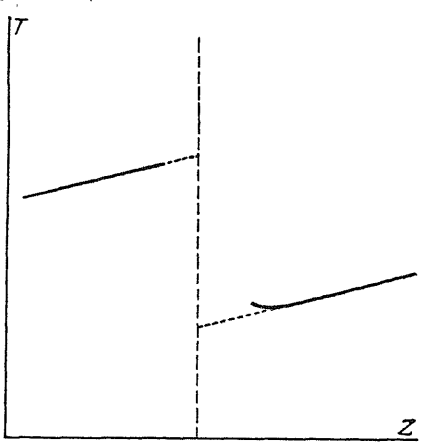

FIG. 23.—Temperature change in a reaction.

(2) *Determination of the Heat of Solution of a Salt.*—The amount of solvent is again 400 gms. of water. The experiment is carried through exactly as described in the determination of the heat capacity. With the help of the drift before and after, the corrected temperature difference is found graphically. Multiplication of this by the heat capacity of the system as found with KCl, gives the value of the heat of solution in cals. Division of this by the number of grams of salt dissolved gives the "specific heat of solution."

(3) *Determination of the Heat of Hydration of a Salt.*—Two portions of crystalline copper sulphate ($CuSO_4 . 5H_2O$) each of 10·00 gms. are weighed out, and the heat of solution of one portion in 396·4 gms. water determined as in the previous paragraph. The second portion is first ground up and then heated in a porcelain basin over a free flame until all the water of crystallisation has escaped and a white powder remains. The anhydrous salt is introduced whilst still hot into the test-tube, which is at once closed by a rubber stopper. After cooling it is weighed. The heat of solution in 400·0 gms. of water is then measured. The difference between the heats of solution of the anhydrous salt and the hydrate gives the heat of hydration. The quantities of water used in the two experiments are different because allowance must be made for the water contained in the hydrate, if the difference between the two heats of reaction is to correspond exactly to the process required, as is made clear by the following scheme:

$$\begin{array}{r} CuSO_4 . 5H_2O + nH_2O = CuSO_4\ (n + 5)\ H_2O + q_1 \\ CuSO_4 . + (n + 5)H_2O = CuSO_4 . (n + 5)\ H_2O + q_2 \\ \hline CuSO_4 + 5H_2O = CuSO_4 . 5H_2O + (q_2 - q_1) \end{array}$$

(4) *Determination of Heat of Neutralisation.*—The heat of neutralisation of $^1/_{20}$ mol of hydrochloric acid wi tha small excess of alkali is measured, and the equivalent heat of neutralisation calculated.

($\alpha\alpha$) *Measurement of the Heat of Reaction.*—Into the Dewar vessel previously used is put 150·0 gms. distilled water and 50 c.c. N/1 hydrochloric acid (taken from the stock solution; the factor is taken into account later on in the calculation of the equivalent heat of neutralisation); the glass stirrer is put in, the copper cover fitted on and the vessel put in the water-bath. Then a thermometer in $^1/_{50}°$ is allowed to hang from a stand by means of string, down into the calorimeter liquid. In a second, smaller Dewar vessel, which remains outside the water-bath, is put 2·2 gms. NaOH or 3·1 gms. KOH (corresponding to a 10 per cent.

excess) and dissolved in 200 c.c. distilled water. When this is completely dissolved another $^1/_{50}°$ thermometer is hung in the solution and stirred round from time to time. The drift is observed in both liquids, stirring as regularly as possible and reading the thermometers at one minute intervals, after tapping. It is best to read the thermometer in (say) the acid at the whole minutes and in the alkali at the half-minutes. For both solutions time and thermometer readings are tabulated. If in both liquids the drift has remained regular for at least five minutes (the drift is not the same for both, since it depends upon the temperatures of the liquids and of their surroundings), then the thermometer is withdrawn from the alkali solution, and the solution is poured through the opening in the cover through which the KCl was introduced before. The time at which this is done is recorded. The quantity of liquid remaining adhering to the thermometer and the small Dewar vessel is usually not more than about $\frac{1}{2}$ c.c. and is determined by re-weighing the emptied vessel. Since originally an excess of alkali was present, the magnitude of the heat of neutralisation is not affected by this loss. After pouring in the solution it is at once vigorously stirred, and after one minute temperature readings are begun. Observations are made every half-minute and recorded in the time-temperature scheme. The readings are continued until the drift has remained constant for ten minutes.

Since the temperatures of the acid and alkali solutions are measured with different thermometers, a comparison of the instruments must be made before the calculation of the result is possible.

($\beta\beta$) *Comparison of Thermometers.*—As a rule it is advisable to carry out the calibration of measuring instruments before beginning an experiment, so that if the instrument happens to be broken, the necessary corrections can be applied to the readings up to that point. But in this particular case, merely for the sake of saving time and labour, this sound custom is departed from, and the calibration of the thermometers done after the experiment, because in this way the calibration can be limited to the small range of temperature important for the experiment.

Bearing in mind that the actual heat of reaction is measured with the thermometer in the acid, the data of the alkali thermometer are referred to the acid thermometer. The comparison is made as follows: the two instruments are tied closely together with string or a rubber band, so that the two mercury reservoirs are at the same level, and hung from a stand so that

the reservoirs dip into water in a 500 c.c. beaker. The temperature of the water should be about 1° lower than that of the alkali solution. Stirring vigorously with a glass rod, the water is gradually warmed up by means of a small luminous Bunsen flame, so that the temperature rises not more than $^1/_{10}$° per minute. The positions of the threads of the two instruments are read, one immediately after the other, every minute, after tapping as far as possible equally strongly, and the readings recorded. The comparison is stopped at a temperature about 1° above the alkali temperature. If the two series of measurements are plotted along one and the same line, then it is easy to read off accurately for every value on the alkali thermometer the corresponding value on the acid thermometer.

($\gamma\gamma$) *Calculation of the Heat of Neutralisation.*—As before (p. 79), time is plotted as abscissæ and the uncorrected temperatures of acid and alkali as ordinates. From the drift before the reaction the temperature is extrapolated for both liquids up to the moment of mixing. The extrapolated alkali temperatures are reduced to temperatures on the acid thermometer by means of the comparison data. The two solutions A and B when mixed have different temperatures t_a and t_b, and the temperature t_m which the mixture would have had, had there been no change by reaction, is calculated by the rule of mixtures. Let A be the weight of acid and B that of the base, c_a, t_a and c_b, t_b the corresponding specific heat and temperatures before mixing, and c_m, t_m those of the mixture produced:

$$A \,.\, c_a \,.\, t_a + B \,.\, c_b \,.\, t_b = (A + B) \,.\, c_m \,.\, t_m.$$

The products $A \,.\, c_a$, etc., represent the heat capacities of the solution. Since we are here concerned with dilute solutions, we can put $c_a = c_b = c_m = c_{H_2O} = 1$.

It follows that

$$t_m = \frac{A \,.\, t_a + B \,.\, t_b}{A + B} \quad . \quad . \quad . \quad (26)$$

The reaction actually starts at the temperature of the mixture t_m calculated in this way. The final temperature is found in a similar way by extrapolating backwards the drift after the reaction to the moment of mixing. The difference between the two temperatures, when multiplied by the heat capacity of the system found in the first experiment, gives the heat of reaction for the neutralisation of $^1/_{20}$ of an equivalent of $H^{\cdot}$ by OH'. When calculating the equivalent heat of neutralisation

the actual factor of the hydrochloric acid used is taken into account.

(2) A Simple Form of Calorimeter

(α) *Apparatus.*—As reaction vessel a 600 c.c. glass beaker is used (see Nernst, "Theoretical Chemistry" (5th English edition, Fig. 40)), standing inside another of about 800 c.c. capacity. On the bottom and the sides of the outer vessel slices of cork are fixed, which ensure a uniform separation of about $\frac{3}{4}$ cm. all round between the two beakers. The layer of still air which thus surrounds the inner reaction vessel is a fairly good insulator and allows only a slow and regular heat interchange with the surroundings. Temperature is measured with a thermometer divided into $^1/_{50}°$. A glass rod with the lower end bent round into a horizontal ring serves as a stirrer. To diminish the heat interchange at the top as much as possible, a wooden cover with holes for thermometer, stirrer, and vessel containing the salt, is put on during the measurement. Before the introduction of the salt to be dissolved, it is contained in a thin-walled test-tube, held in position in the proper opening in the wooden cover; the lower end, slightly greased, dips far enough into the calorimeter liquid for temperature equalisation between salt and solvent to occur.

(β) *Experimental Procedure.* (1) *Calculation of the Heat Capacity.*—The heat capacity of the whole system is calculated additively from the heat capacities of its separate parts:

Heat capacity of calorimeter beaker = wt. of beaker × sp. ht. of glass. (0·19.)

Heat capacity of liquid = wt. of liquid × sp. ht. of water. (1·0.)

Heat capacity of stirrer = wt. of stirrer × sp. ht. of glass.

Heat capacity of thermometer: this is calculated by means of the coincidence that equal volumes of glass and of mercury have the same heat capacities (1 c.c. = 0·47 cal.). The volume in question is found by dipping the bulb into a measuring cylinder containing water and reading the change of level.

(2) *Heat of Solution of a Salt.*—The salt is ground to a fine powder (without previous drying) and weighed in the test-tube on an analytical balance to 1 mgm. (After introducing the salt into the calorimeter the test-tube is carefully dried outside and re-weighed.) About 300 gms. of distilled water is weighed into

the calorimeter vessel with an accuracy of $^1/_{10}$ gm. It is then placed in the jacketing vessel, the stirrer and thermometer put in place, and the wooden cover put on; the test-tube with the salt (closed by a cork) is fastened into the proper opening in the cover. The thermometer is hung from a stand so that the bulb is well in the water. After assembling the apparatus about ten minutes is allowed for the temperature of the salt and the water to equalise. The procedure is then the same as before (p. 78 to p. 79).

The value of the heat of reaction in cal. is found by multiplying the corrected temperature difference by the heat capacity as calculated in (1). On dividing by the number of grams of salt dissolved, the "specific heat of solution" is obtained.

(3) *Heat of Neutralisation.*—Into the calorimeter vessel is put 150·0 gms. water and 50·0 c.c. $\frac{N}{1}$ hydrochloric acid (from the stock solution; the actual factor is introduced later in the calculation of the equivalent heat of neutralisation). The stirrer and wooden cover are put in place and the thermometer suspended inside by a string from a stand. The alkali solution is in a small conical flask or, better, in a small Dewar vessel. The remainder of the procedure is as described already (pp. 81 *seq.*).

(3) Testing a Thermometer

In an ordinary laboratory thermometer, as purchased, nowadays, irregularities in the capillary need scarcely be considered as a cause of inaccuracies; the most important are various alterations in volume undergone by the bulb of the thermometer, which take place more or less rapidly depending upon the manufacture and the use made of the thermometer. Two main kinds of such volume change can be distinguished: (1) an irreversible change, consisting of a slow contraction which persists for a long time and causes a gradual rise in the readings of the thermometer. (2) Reversible and more rapid volume changes which appear on changing from one temperature to another. The effect of these is that after warming strongly the bulb does not immediately return to its original volume, but for a certain time it remains expanded; likewise after strong cooling the bulb tends to remain too small. In the first case the indications of the instrument are too low, in the second, too high. In the course of time the original volume re-establishes itself—always much more quickly than the slow process of contraction mentioned under (1). When making accurate measurements of

absolute temperatures (as distinct from temperature differences), it is therefore absolutely necessary to test the accuracy of the thermometer to be used. This is done either by checking the zero—or 100°—point, or by a comparison with a thermometer calibrated at the National Physical Laboratory, or a "Normal" thermometer calibrated at the Reichsanstalt.

(α) *Checking the Zero-point.*—A large quantity of distilled water is frozen in a large porcelain basin by surrounding it with a freezing mixture. The ice produced is broken up and poured into a thick glass beaker of at least 10 cm. diameter, with just so much distilled water that the mixture can be stirred conveniently. Instead of the ice, in winter freshly fallen clean snow may be used. Ice from the factory is of no use since it is usually contaminated by salts and therefore has too low a freezing temperature. The thermometer is hung from a stand at such a height that the bulb dips into the ice-water mixture and the zero-point of the scale is at least 2 or 3 cm. below the surface. After stirring for a few minutes with a vertical stirrer (a glass rod, the lower end of which is bent round into a loop) the thermometer, held by the upper end, is raised until the position of the thread can just be read with a lens. The place at which the reading is taken is tapped at the back with an empty thermometer case. The measurement is repeated and the reading recorded, at least four times. Between the measurements the thermometer is left for a few minutes in the ice, which is well stirred. The mean of all the observations is taken.

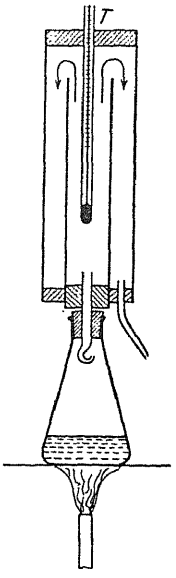

FIG. 24.

If the position of the thread is above the zero of the scale, the amount of the discrepancy must be subtracted from all the indications given by the instrument, and vice versa.

(β) *Checking the* 100°*-point.*—The apparatus shown in section in Fig. 24 is suitable and is easily constructed from ordinary laboratory materials. Distilled water is heated to boiling in a conical flask. The vapour rises up through a glass tube bent round at its lower end (to prevent spray coming in contact with the thermometer bulb directly) into a wider tube, into which the thermometer projects as far as a point several degrees above the 100° mark. This tube is surrounded by a wider one held

concentrically round it by means of a cork ring. The outer tube is a few centimetres longer than the inner, and is closed at the top by a cork bung through which the thermometer is inserted. The vapour passes up to the top of the inner tube and down the outer to a hole in the lower cork ring through which it escapes together with condensed water. The double jacket of vapour ensures the maintenance of the exact boiling temperature in the inner tube. The droplets of condensed water which at first cover the tubes disappear after a time, when the tubes have reached the temperature of the vapour. The reading is taken when a constant temperature is reached. It should be recalled that the boiling-point of water is 100·00° only under the standard barometric pressure of 760 mm. For lower pressures cf. the table on page 35.

(γ) *Comparison with a Standard Thermometer.*—This is done exactly as the comparison of two calorimeter thermometers described on page 81. For most purposes it is sufficient to compare every 10°. For temperatures above 100° an oil-bath is used. Before the comparison the ice point of the standard thermometer is checked as described above. The temperatures read directly on the standard thermometer are corrected by the table of corrections which is sent out with every thermometer calibrated at the N.P.L. or the Reichsanstalt. Also the correction for exposed stem which is discussed below must be applied for both thermometers.

(δ) *Correction for Exposed Stem.*—Accurate thermometers are so calibrated that the temperature indications are correct only when the whole of the mercury thread is at the temperature in question. In many measurements only the bulb and a part of the mercury thread are at the temperature which is being measured. The exposed part of the thread is then too long or too short, according to whether its temperature (usually the same as the room temperature) is above or below the temperature which is being measured. (The thread temperature can be checked by a small auxiliary thermometer hanging near the middle of the exposed portion of the thread.) The correction amounts to $^1/_{6000}$° per degree of exposed stem and per degree difference between the mean temperature of the thread and the temperature to be measured, for thermometers of ordinary glass. With a measured temperature t, a mean temperature of the thread t_m and n degrees of exposed stem the correction is

$$+\frac{n(t-t_m)}{6000} \quad . \quad . \quad . \quad . \quad (27)$$

Example: Thermometer reading 200·0°. Thread temperature 27°. The thermometer is at the measured temperature up to the graduation 30°.

$$\text{Correction} + \frac{170 \cdot 173}{6000} = + 4{\cdot}9^\circ.$$

$$\text{True temperature} = 200 + 4{\cdot}9 = 204{\cdot}9^\circ.$$

The correction for the exposed stem can only be ignored when small *differences* of temperature are being measured, or when a comparison is made under exactly the same external conditions: the same number of degrees exposed and the same thread temperature, which is nearly the case when a comparison is being made of two similarly constructed thermometers.

IX. METALLOGRAPHY

A. CALIBRATION OF A THERMOCOUPLE

(a) Theory

If two wires, of different metals (pure metals or alloys) are soldered together at the ends and the two joints are at different temperatures, then an electrical potential difference is set up between them, depending in magnitude upon the nature of the wires and the difference in temperature. The "thermo-elements" which depend upon this phenomena are of the greatest importance in temperature regions (very high and very low temperatures) where the mercury thermometer cannot be used.

With the usual combinations the thermal E.M.F. set up is of the order of magnitude of about 1 to 5 millivolts per 100° temperature difference between the junctions. Hence, a sensitive millivoltmeter is used as the measuring instrument. The millivoltmeter is connected in the current circuit as follows: the wires of the thermocouple are directly welded together at one end only; at the other end they are soldered to copper wires which lead to the terminals of the measuring instrument.[1] If the two soldered joints to the copper wires are kept at the same constant temperature—say in melting ice—then this arrangement acts as though the two thermocouple wires were directly connected together at this place and were at 0°. According to the principle of the "thermo-electric series," the magnitude of the thermal E.M.F. in this circuit depends only upon the two metals whose ends are at different temperatures, and not upon the nature of the conductor by which the two metals are connected together.

The connexion between thermal E.M.F. and temperature difference can often be expressed satisfactorily, over the temperature range which is most usually of importance, by a quad-

[1] If these terminals are of copper, no further thermal E.M.F. is produced here. But with other metals, e.g. with brass terminals, there may be, if the terminals are not both at the same temperature; at the same temperature these effects cancel out. It is advisable therefore to wrap some wadding round the terminals.

ratic equation. With many combinations—e.g. iron-constantan—the relationship is almost linear over several hundred degrees.

For the most commonly used combinations (platinum-platinum rhodium ; iron-constantan (Ni-, Cu-, Zn-alloy) ; copper-constantan) measuring instruments may be purchased, the scales of which, instead of indicating millivolts indicate temperature degrees directly, provided that one of the junctions is at 0°. It is advisable, however, to calibrate the scale again with the aid of accurately known fixed thermometric points, or at least to check the accuracy of the temperature indications of the purchased instruments. For this purpose the melting- or boiling-points of definite chemical substances are suitable.

References :—
Eucken, Jette, and Lamer. § 370.
Ostwald-Luther, p. 586.

(b) Experimental

In the following experiments an iron-constantan couple is used ; this has a range of up to about 600° C. Useful fixed points for its calibration are the following boiling-points :

	Boiling-point at 760 mm.	Lowering of the B.P. per 1 mm. Lowering of Pressure.
Water . . .	100·00°	0·04°
Naphthaline . .	217·68°	0·06°
Diphenylamine . .	302·2°	0·09°
Sulphur . . .	444·55°	0·09°

In addition the melting-points of pure cadmium and pure zinc can be used :

Melting-point of cadmium . . . 320·9°.
" " " zinc . . . . 419·4°.

(1) By Boiling-points

The experimental arrangement will be understood from Fig. 25. The heating of the water, naphthaline, or diphenylamine is done in an ordinary distilling flask of about 100 c.c. capacity. It is advantageous to bend the side tube upwards. To insulate the thermocouple wires from each other, a thin hard-glass capillary is drawn over them for a distance of about 20 cm. up from the junction. Beyond the heated part the insulation is continued with thin rubber tubing, or

bored glass beads, or short pieces of glass tubing. To protect them against chemical action by the vapours or the melts, the junction and the two wires are put into a narrow sheath of hard glass sealed at the lower end. For higher temperatures porcelain tubes or fused silica tubes are used.

The junction protected in this way is fastened in position in the flask (by means of a cork) so that it comes about 1 cm. above the surface of the boiling liquid and the vapour surrounds the sheath up to about 5 cm. or 6 cm. The latter point is important, otherwise the junction will be cooled by conduction up the wires and will be at too low a temperature. The flask is shielded from draughts by means of a cubical asbestos box (not shown), and heated through an asbestos sheet until the vapour streams out of the side tube. The other two junctions are put into a Dewar vessel containing a mixture of ice and water. The connexions to the millivoltmeter are made so that the copper wire soldered to the iron wire is connected to the positive terminal. Errors of parallax in reading are avoided by the aid of the mirror on the scale. With each substance, the position of the pointer is read three times at intervals of about three minutes, the boiling being continued all the time. The pointer reading must remain practically constant.

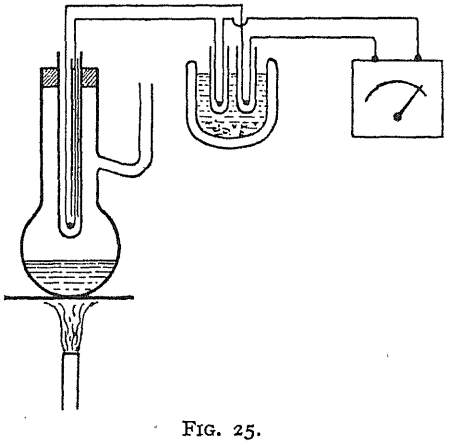

FIG. 25.

The boiling-point of sulphur is determined in a hard glass test-tube, about 15 cm. long and 1·5 cm. diameter. Flowers of sulphur is put into a depth of about 2 cm., and the junction put about 10 cm. down the tube, which is held by its upper end in a clamp, and inclined at an angle of 45°. The tube is heated at the lower end by a small luminous flame. The sulphur vapour creeps up inside the tube and surrounds the wires for several cm. above the junction. Currents of air are prevented as far as possible by a suitable asbestos shield. Here again the setting must remain practically constant. At the end of the experiment the sulphur is allowed to solidify in an inclined position,

otherwise the tube breaks. The barometric height is read before and after the calibration.

(2) By Melting-points

The determination of melting-points involves the observation of freezing curves. The metal is placed in a tube of iron, or hard glass (or, with high-melting metals, in tubes or crucibles of hard porcelain, graphite, or fire-clay), and melted in an electric oven which is connected to the main leads, with a suitable resistance and ammeter and switch in circuit. As soon as it is liquid the thermocouple is fixed in position in the melt, as nearly as possible centrally, by means of a bored cork in the open end of the melting tube. To prevent compression of the glass, porcelain or silica sheath by the solidifying metal, the sheath is placed in a thin-walled ($\frac{1}{3}$ mm.) seamless steel tube closed at the lower end. This fits the sheath closely, and when dipped into the melt, should project several centimetres above the surface. (In the case of cadmium and zinc considered here, there is no danger of alloy-formation with the iron.)

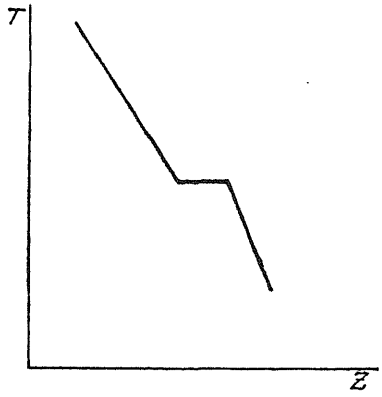

Fig. 26.—Cooling Curve.

The heating current is now switched off, and the melt cools slowly and regularly. The reading of the millivoltmeter is noted every half-minute. From the observations time-temperature curves are constructed, by plotting on a sufficiently large scale as ordinates, the temperature, i.e. the millivoltmeter readings (T) and as abscissæ the time (Z), as in Fig. 26. Drawing a line through the points, a curve is obtained which falls steeply over the greater part of its course, but remains horizontal during the freezing process. The scale reading at this point corresponds to the melting-point required. If super-cooling occurs, the steeply falling part of the curve is followed first by a slight rise, and then by the horizontal portion (see pp. 22 and 25).

At the end of the experiment the metal is fused again and the thermocouple with its protecting sheaths withdrawn.

(3) The Calibration Curve

The millivolt readings are plotted as abscissæ against the corresponding boiling- or melting-temperatures (after applying the corrections for the barometric heights). On joining up the points an almost straight line is obtained, showing that for an iron-constantan couple there is approximate proportionality over this temperature range between temperature difference and thermal E.M.F. With a silver-nickel couple, on the other hand, the line is distinctly curved.

B. COOLING CURVES OF ALLOYS

(a) Theory

(1) The Melting-point Diagram

The problem discussed here is the investigation of four different alloys of Cd and Zn. The relationships in the case of Cd and Zn are particularly simple since the two molten metals are completely miscible, and in the solid state neither mixed crystals nor a solid compound is formed. The thermal behaviour of Zn-Cd alloys is represented by the freezing-point diagram shown in Fig. 27A. If to pure molten Zn (left-hand ordinate: 100 per cent. Zn) increasing quantities of Cd are added, then the freezing-point of the Zn (i.e. the temperature at which pure Zn begins to separate from the melt and is therefore in equilibrium with the melt) is more and more lowered—approximately in proportion to the amount added. The line AE represents this behaviour. Analogously the freezing-point of pure Cd (right-hand ordinate: 100 per cent. Cd) is lowered by addition of Zn, corresponding to the line BE. At the point E—the *eutectic point*—both melts crystallise out from a melt of this composition; this happens in a quick, rhythmic alternation, since the crystallising out of a small quantity of Zn causes supersaturation with respect to Cd and hence separation of this metal, and this in a short time has the same effect with respect to Zn. This rhythmic alternation of crystallisation causes the lamellated structure frequently seen in the eutectic mixture under the microscope, after proper treatment of the solidified regulus (grinding, polishing, etching).

If an alloy of, say, the composition G is heated to a temperature T_a such that it is completely molten, and the melt is allowed to cool by radiating heat away, then if the falling temperature is followed with a thermocouple the behaviour of

the system is as follows : as long as the melt is present alone, the cooling proceeds at a fairly uniform rate. In a time-temperature curve (Fig. 27B) this section consists of a line of almost constant slope (T_aT_k). From some definite temperature T_k onwards there is an obvious decrease in the rate of cooling. This arises from the fact that with the temperature T_k the point is reached at which solid Zn begins to crystallise out of the melt of this composition. The heat of solidification now set free partially compensates for the loss of heat by radiation. As the Zn crystallises out the composition of the melt changes in the sense of becoming poorer in Zn and richer in Cd. In such alloys the freezing-out point of the Zn is lower ; the temperature therefore falls further, corresponding to the line T_kE (Fig. 27A), and through the further crystallisation of Zn the alloy continues to become

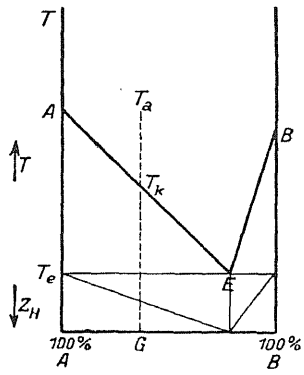

FIG. 27A.—Freezing-point diagram.

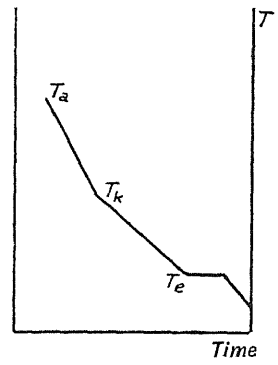

FIG. 27B.—Cooling curve.

richer in Cd. This second phase of the cooling process gives on the time-temperature diagram (Fig. 27B) a line of smaller slope than the first. The point T_k in diagram (A) corresponds in (B) to the discontinuity where the lines T_aT_k and T_kT_e meet. Finally at the point E (and T_e) the composition of the eutectic mixture is reached and the whole melt freezes without further change in composition. This freezing of the eutectic mixture resembles the freezing of a pure substance, and takes place at constant temperature. In the time-temperature diagram there is a "halt." When the whole is solid, the further loss of heat is accompanied by a lowering of temperature.

Frequently there is a short halt at the point T_k, or even a slight warming up, which is caused by super-cooling (p. 91), the removal of which allows so much of the one component to

crystallise out that the heat set free exceeds what is being removed by the cooling.

If the melt has originally the composition of the eutectic mixture, there is no break in the cooling curve followed by a slower rate of cooling as at T_k; instead the behaviour resembles that of a pure metal (cf. Fig. 26 above) in which the period of regular cooling is followed by a long halt, whilst the freezing is taking place, and this in turn is followed by the regular cooling of the solidified melt.

The following method is also very important for finding the eutectic point: the *same quantity by weight* is taken of alloys of the same components but of different compositions, and the *duration of the halt at the eutectic temperature* is noted. This is longest for the alloy with the composition of the eutectic mixture, being shorter for all others because a part of the melt has already been separated out of the system in the form of the component which crystallises out. Thus on plotting (in the diagram, Fig. 27A) the alloy composition on the abscissa axis and as ordinates from the line T_eE downwards the duration of the halt (Z_H), there results a triangle the apex of which is at the eutectic composition.

(2) The Melting-point Diagram and the Phase Rule

The phase rule states: Number of degrees of freedom + Number of phases = Number of components + 2:

$$F + P = C + 2.$$

In the system we have considered there are two components: Zn and Cd. This is the smallest number of substances by which the composition of all the phases can be expressed. Above AEB is the region of the homogeneous melt; here there is only the liquid phase present: $P = 1$; $F = 2 + 2 - 1 = 3$; in other words, within this region pressure, temperature, and concentration can be altered at will without causing a phase to disappear or a new one to appear. Since the freedom in respect of pressure is annulled by working always under atmospheric pressure, only the temperature and concentration remain variable.

Along the line AE or BE solid Zn or solid Cd coexists with the melt. Accordingly $P = 2$ and $F = 2 + 2 - 2 = 2$. Of these two degrees of freedom, the pressure, for the reason already given, can no longer be chosen at will. There remains only one degree of freedom; when the temperature has been decided,

then the concentration, i.e. the composition of the melt, is definitely fixed. Conversely if the composition of the melt is given, freezing-out begins at a definite temperature.

At the point E the liquid melt is in equilibrium with the solid eutectic mixture, and here it is immaterial whether the total composition of the solidified mass is the same as that of the eutectic mixture, or whether an excess of Zn or Cd is present. The eutectic mixture is a mechanical mixture of solid Zn and Cd. (There are no mixed crystals formed.) Hence $P = 3$, $F = 1$. This one degree of freedom is removed by working at atmospheric pressure: hence both temperature and composition are uniquely determined at the eutectic point. Change of pressure alters the eutectic temperature. Experiment shows also that the composition of the eutectic mixture alters in a continuous manner with the pressure, thus proving that the eutectic mixture is not a chemical compound.

References :—
Eucken, Jette, and Lamer. §§ 160-63 ; 173.
Nernst. Bk. III, Chap. III ; Bk. IV, Chap. II, pp. 701 *seq.*, 716 *seq.*

(b) Experimental

(1) The Cooling Curves

The cooling curves are taken for four (previously prepared) alloys, of composition in weight per cent. as follows :

1. 45 per cent. Zn ; 55 per cent. Cd.	2. 30 per cent. Zn ; 70 per cent. Cd.
3. 18 „ Zn ; 82 „ Cd.	4. 10 „ Zn ; 90 „ Cd.

In addition, the cooling curve of an alloy of unknown composition should be determined. The experiment is done as already described (p. 91) for the calibration of the thermocouple by means of the melting-points of Zn and Cd. The alloys are placed in hard glass tubes sealed at the lower ends and numbered ; these are placed in an electric furnace connected to the current leads as already described. After fusion of the metal, the thermocouple with the two protecting tubes is fixed centrally in position by means of a bored cork. The contents of the tube are well stirred with the protecting tube of the thermocouple, to remove any inhomogeneities in the alloy produced in the previous solidification. After switching off the furnace current the pointer reading is noted every half-minute (to the nearest second, if possible—the watch should be placed *on* the millivoltmeter). The more accurately the

readings are timed, the more regularly the curves should run. Draughts, especially from the door, should be avoided, as they disturb the regular cooling of the furnace. The scale readings and the actual time are tabulated. The experiment is ended at 200°; it is repeated in the same way exactly, and taking the same precautions, with each of the alloys. The millivoltmeter should be left in the same place throughout the experimental work (taking the fixed points and the cooling curves) to avoid changes of the zero of the instrument.

(2) Construction of the Temperature-time and the Melting-point Diagrams

The experimental data are plotted on temperature-time diagrams (cf. Fig. 27B): abscissæ: actual time; ordinates: scale readings. The scale readings corresponding to the first discontinuity and the halt at the eutectic point are in each case converted into temperatures. The melting-point diagram is constructed from the melting-points of pure Zn and pure Cd, the points of discontinuity (T_k) and solidifying-point of the eutectic (T_e); it is an advantage to take the same unit for the ordinates as in the temperature-time diagram. The composition being known in the case of alloys 1 to 4, the points T_k must lie upon the vertical lines from the abscissa axis at the appropriate percentage ratio. With Zn-Cd alloys the freezing-point of Zn is lowered by an amount almost exactly proportional to the amount of Cd, so that the line joining the freezing-points of Zn in alloys of increasing Cd content is almost straight. Thus the composition of the eutectic mixture can be found sufficiently accurately by drawing a line through the ordinate T_e parallel to the abscissa axis, and prolonging the straight line joining the melting-point of pure Zn and the various T_k points until it cuts this parallel. If now the T_k point of the unknown alloy is put on to this diagram, the corresponding abscissa gives at once its composition.

On the diagram, as in Fig. 27A, are also plotted the durations of the halt in the case of the four known alloys. These should indicate the same composition for the eutectic as the temperature measurements.

C. PREPARATION OF METALLOGRAPHIC SECTIONS AND THEIR MICROSCOPIC EXAMINATION [1]

(1) Grinding

The alloy, of which the composition has just been determined by taking its cooling curve, is freed from the glass tube and by means of a metal-saw a piece is sawn off about $\frac{1}{2}$ cm. long. A surface is then worked by using a coarse file followed by a finer, the surface being filed as even as possible. The sharp edges and corners must be carefully blunted with the file. (Instead of working with a file, grinding with an emery wheel leads to the same result more quickly; in this case heating of the metal, which under some circumstances can result in a change in the structure, is avoided by dipping it in cold water frequently.) The filed surface is now prepared for polishing by rubbing it on emery paper. For this purpose strips of emery paper (*ca.* 20 cm. long, 6 cm. wide) are laid upon a hard base, e.g. a glass sheet. The sample, held between the fingers, is rubbed to and from with a light pressure, tilting the section as little as possible when changing its direction of movement, in order to avoid rounding the edges. The grinding is continued until no grooves can be seen with a lens, except the parallel scratches produced by the paper. A coarser paper is used in this way first, followed by a rather finer; when using a new paper the sample is turned through 90°, so that the new scratches cross the old at right angles. In this way it is easy to decide when the coarser grooves have been removed. On finishing with the finest emery paper the surface must give a brilliant reflected image of a lamp or of the window; under the lens only very fine scratches should be visible.

A succession of emery papers is used, starting with the coarser and working up to the finest grain.

(2) Polishing

This is done by a gentle pressure of the emery-ground surface against a rapidly rotating polishing wheel. This is a metal or wooden wheel with a hard rubber surface carrying a suitable polishing cloth tightly stretched upon it. *Polishing is always done with the cloth damp.* For this purpose an aqueous suspension of the finest polishing powder (specially prepared alumina) is sprayed on to the rotating wheel from a well-shaken

[1] For further information see P. Goerens, "Introduction to Metallography," Longmans & Co.

spraying-flask. The excess water is thrown off by centrifugal force and caught by the guard, and is collected in a vessel placed underneath. When the polishing powder on the surface of the metal which is being polished begins to stick, it is a sign that the cloth is too dry. By inspection from time to time with a hand lens the gradual disappearance of the marks of grinding can be followed. When this is finished, the polished surface is carefully washed with water, without touching it with the fingers, and dried cautiously between clean pieces of filter paper.[1] In general, such a surface is still unsuitable for microscopic observation. To make the structure visible, a treatment by etching is required.

(3) Etching

The sample of metal is laid with the polished side upwards in a glass vessel filled with a suitable etching material. For present purposes a solution of 1 per cent. concentrated nitric acid in 99 per cent. alcohol is suitable. The sample is left in the bath until the surface shows a slight dullness. The sample is then washed with distilled water, dried between filter papers and examined under the microscope.

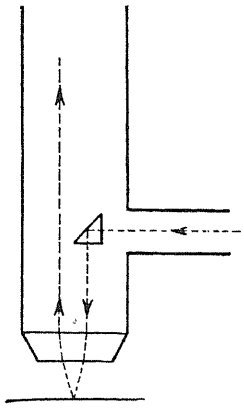

Fig. 28.—Vertical illuminator.

(4) Microscopic Examination of the Section

For detecting the structure the polished surface is investigated microscopically in vertically incident and reflected light. For this purpose a "vertical illuminator" is used, either introduced into the microscope tube or screwed in between the tube and the objective; the action of this is obvious from Fig. 28.[2]

In order that the metal surface shall really be perpendicular to the optical axis of the microscope, it must be adjusted horizontally. The adjustment is made by the following device: the section with the smooth surface downwards, is placed upon

[1] Residual traces of polishing material, or any grease, easily produce an incomplete etching, which can lead to quite erroneous conclusions in the consideration of the structure and composition of the alloy.

[2] Instead of the totally reflecting prism, a reflecting glass disc inclined at 45° can be used.

a carefully cleaned glass or metal sheet. A brass ring of suitable height is now laid round it, and a small lump of plasticine put on the sample. An ordinary microscope object-glass is now pressed on to this, until it meets the brass ring all round (Fig. 29). The object-glass with the sample now adhering firmly to it is removed, turned over and placed on the microscope; no further adjustment is required. The illumination (for observation through the microscope) is obtained by means of a 4-volt glow lamp (pocket lamp bulb) operated by two accumulators, which is placed against the diaphragm of the vertical illuminator; and for observation on a white cardboard screen, and for photography, the light of an arc lamp is concentrated on to the iris diaphragm. The magnifications are obtained from the tables in the microscope case; usually about a hundred-fold is convenient.

The identification of the structure is based upon the consideration that as a result of the etching by nitric acid, which attacks the zinc more quickly than the cadmium, the former appears black in reflected light (because it is roughened) and the latter appears bright.

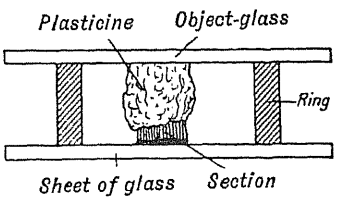

FIG. 29.

With sample No. 1 containing 55 per cent. of Cd, only the primary zinc crystals are seen in the section; the structure of the eutectic is not recognisable; possibly the crystallisation force of the zinc is so large that in addition all the zinc of the eutectic is "moulded" into the same form. The parts between the crystals must therefore consist of pure cadmium.

Sample No. 2 with a 70 per cent. content of cadmium shows clearly the dendritic primary zinc crystals, with a rather coarse eutectic between them.

Sample No. 3 represents a fairly pure eutectic (82 per cent. Cd) having partly a very fine lamellar structure, the latter showing particularly clearly at the boundary lines of the crystallites.

Sample No. 4 with a content of 90 per cent. Cd shows clearly primary Cd crystals in addition to a somewhat darker eutectic; a lamellar structure is often visible as well.

Kinetic measurements

General Remarks

(1) *Dependence of Reaction Velocity upon Concentration.*—The rate at which different chemical reactions take place depends not only upon the nature of the reactants but also upon a number of other factors, such as the temperature, the concentration, the solvent and the presence of foreign substances (catalysts). For reactions in which the change involves the union of two or more molecules the influence of concentration is easily understandable. The reaction can only occur when the molecules collide together; the reaction velocity, i.e. the amount changed, or the change in concentration, in unit time, depends upon the number of collisions. According to the laws of probability, this is proportional to the product of the concentrations of the individual reactants. For the formation of hydrogen iodide in the gaseous state, which takes place according to the equation

$$\underset{c_1}{I_2} + \underset{c_2}{H_2} = 2HI$$

the velocity of the reaction from left to right is expressed by the change in iodine or hydrogen concentration occurring in unit time:

$$-\frac{dc_1}{dt} = -\frac{dc_2}{dt} = k \,.\, c_1 \,.\, c_2 \qquad . \qquad . \qquad (28)$$

For reactions in which, according to the equation of the reaction, only one molecule undergoes change, as for example, in the decomposition of gaseous N_2O_5

$$N_2O_5 = N_2O_3 + O_2$$

we have, by formal analogy with (28), the expression

$$-\frac{dc_1}{dt} = k \,.\, c_1 \quad . \qquad . \qquad . \qquad . \qquad (29)$$

This is in agreement with the actual course of the reaction, and is interpreted physically as follows: in such reactions, where the collision of molecules is apparently not necessary for the change, it would be expected, *if all the molecules are in the same state*, that at any given moment either all the molecules would react, or none. The fact that these reactions also take place over an interval of time, conforming to equation (29) can only be explained by the assumption that the molecules are not all

in the same state at the same time, but that always a certain number differ from the rest in that they are in an *active state*, in which they are able to react. Now according to the laws of probability, if there are a great many molecules present, then the number of these which are in the active state, and therefore also the number which react in unit time, is proportional to the total number of all the molecules. That is

$$-\frac{dN}{dt} = k \,.\, N \quad . \quad . \quad . \quad . \quad (30)$$

Since $\frac{N}{v} = c$, where v is the volume, then on division of equation (30) by v

$$-\frac{dc}{dt} = k \,.\, c.$$

So that in reactions of this kind also the dependence of the reaction velocity, i.e. of the number of molecules reacting (or the change in concentration) in unit time, upon the absolute number of molecules present (or concentration) is understandable.

Reactions for which a collision between two molecules or three molecules is necessary in order that the change shall occur are called bi- and termolecular reactions, respectively. Reactions of the kind which has just been discussed, where according to the equation of the reaction only one molecule is changed, are called monomolecular reactions.[1] A comparison of the number of collisions (calculated from kinetic theory considerations) and the number of molecules actually reacting, shows that with bi- and termolecular reactions also by no means all the collisions are fruitful, so that here also it is essential to the change that the collisions shall be between molecules in the active state.

(2) *Unimolecular Reactions.*—The typical example is a radioactive decomposition, which follows equation (30). Since it is a question of the decomposition of radioactive *atoms*, N represents the number of atoms. The process is therefore monatomic. From (30) the velocity constant is

$$k = -\frac{dN/N}{dt}.$$

It represents the fraction of the number of radioactive atoms present at any given moment which decompose in unit time,

[1] There are, however, some reactions which are *kinetically* bimolecular, although the chemical equation involves one molecule only—e.g.

$$CH_3 \,.\, CHO = CH_4 + CO.$$ —[Trs.]

provided that dt is chosen so small that N remains practically constant during this time unit. The calculation with c instead of N is analogous, and all the following formulæ for N apply similarly for c. k has the dimensions $\frac{1}{\text{time}}$. If therefore a larger time unit is chosen, say minutes instead of seconds in the description of a given process, k has a correspondingly larger value. Integration of (30) gives for the amount changed during a longer interval of time

$$-\int\frac{dN}{N} = -\int d\log_e N = k\int dt,$$

or

$$-\log_e N = kt + C \quad . \quad . \quad . \quad (31)$$

Writing down the number of atoms corresponding to two different times, then the amount of change taking place between the two moments in time is obtained by subtraction of the upper of the two following equations from the lower:

$$\begin{array}{r} -\log_e N_1 = k\,.\,t_1 + C \\ -\log_e N_2 = k\,.\,t_2 + C \\ \hline \log_e N_1 - \log_e N_2 = \log_e \frac{N_1}{N_2} = k(t_2 - t_1). \end{array} \quad . \quad (32)$$

The more convenient decimal logarithms are usually employed in the calculation. Equation (32) then takes the form

$$\frac{\log_{10} N_1 - \log_{10} N_2}{0{\cdot}4343} = k(t_2 - t_1). \quad k = \frac{\log_{10} N_1 - \log_{10} N_2}{0{\cdot}4343\,(t_2 - t_1)} \quad (33)$$

Often the time at which observation of the course of the reaction is begun is called 0 and the corresponding number of atoms N_0, so that equation (32) becomes

$$\log_e N_0 - \log_e N_t = k\,.\,t\,;$$

and equation (33)

$$\frac{\log_{10} N_0 - \log_{10} N_t}{0{\cdot}4343} = k\,.\,t. \quad 0{\cdot}4343\,k = \frac{\log_{10} N_0 - \log_{10} N_1}{t}.$$

Equations (32) and (33) have the form of the equation of a straight line:

$$y_1 - y_2 = k(x_2 - x_1)$$

in which $y = \log_e N$ or $\log_{10} N$ and $x = t$. k or $0{\cdot}4343k$ is then the tangent of the angle which the straight line makes

with the abscissa axis, and is therefore the ratio of the change in the natural or the decimal logarithm of the number of atoms, to the length of time required for this change.

If instead of plotting the logarithm of the number of atoms against time, the number itself, or some quantity proportional to it (e.g. the activity, see p. 111) is plotted, a logarithmic curve is obtained (Fig. 30). The characteristic feature of this is that the *amount* decreases geometrically (1; $\frac{1}{2}$; $\frac{1}{4}$; $\frac{1}{8}$; $\frac{1}{16}$; $\frac{1}{32}$; $\frac{1}{64}$), whilst the time increases in arithmetic progression (1; 2; 3; 4; 5; 6).

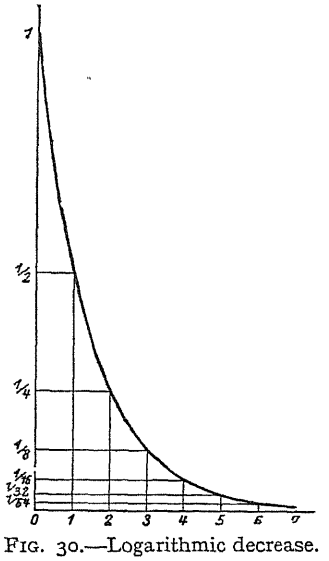

FIG. 30.—Logarithmic decrease.

The time required for a given amount (N) of a radio-element to decrease to one-half is called the "Half-value period" (t_h). The character of a radio-element is usually expressed by this quantity rather than by the corresponding decomposition constant. The connexion between the half-value period and the decomposition constant is obvious from (32), if $N_0 : N$ is put equal to $2 : 1$:

$$t_h = \frac{\log_e 2}{k} = \frac{\log_{10} 2}{0{\cdot}4343k} = \frac{0{\cdot}693}{k} \quad . \quad . \quad (34)$$

Equation (32) can also be written in the form

$$\log_e \frac{N_2}{N_1} = -k(t_2 - t_1);$$

so that

$$N_2 = N_1 \,.\, e^{-k(t_2 - t_1)}$$

or

$$N_t = N_0\, e^{-kt} \quad . \quad . \quad . \quad . \quad (35)$$

(3) *Bimolecular Reactions.*—As has already been mentioned, these reactions differ from monomolecular reactions in that it is an essential condition for reaction that one molecule shall collide with another. It depends upon the kind of reaction, whether the collision is between two similar or two different molecules. The formation of hydrogen iodide

$$H_2 + I_2 = 2HI$$

and its decomposition

$$2HI = H_2 + I_2$$

are both typical bimolecular reactions; in the first case different molecules collide, in the second, similar molecules.

Equation (28) shows that the constant $k = -\frac{dc_1/c_1}{dt} \cdot \frac{1}{c_2}$ has the dimensions $\frac{1}{\text{Time}} \cdot \frac{1}{\text{Concentration}}$. (Thus differing from the constant in a monomolecular reaction.) In this case, therefore, the numerical value of k depends not only upon the time unit selected, but also upon the concentration unit.

Bimolecular reactions *in which the concentration of one of the reactants*, e.g. c_2, *is very large in comparison with the other* (c_1), take place, since c_2 remains practically constant, as if the reaction velocity depended upon c_1 only, that is, they resemble monomolecular reactions. Examples of this are the inversion of cane sugar, and the hydrolysis of methyl acetate in dilute aqueous solution:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$
$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_3OH.$$

The course of such a reaction can obviously be represented by equations (32) or (33).

Concerning the temperature coefficient of reaction velocity, see page 3.

References :—
Eucken, Jette, and Lamer. §§ 230-34; 255, 256.
Nernst. Bk. III, Chap. V; Bk. IV, Chap. IV.
H. S. Taylor. Chap. XIV.

X. THE TRANSFORMATION OF RADIO-ELEMENTS

(a) General remarks

THE break-up of a radio-element is a typical monomolecular reaction. It is usually investigated with an electroscope by measuring the ionising action of the rays emitted by the radio-element. The following exercise is the study of the decomposition of the active deposit (actinium B with its disintegration products) formed from actinium emanation (AcEm). The formation of this active deposit takes place according to the scheme:

$$\text{Actinium (Ac)} \xrightarrow{(\beta)} \text{RdAc} \xrightarrow{(\alpha)} \text{AcX} \xrightarrow{(\alpha)} \text{AcEm} \xrightarrow{(\alpha)} \text{AcA} \xrightarrow{(\alpha)} \text{AcB}$$

20y 19d 11d 3·9s 0·002s 36·1m.

(The half-value period is written underneath the symbol of each element.) In the formation of AcB from Ac, α and β rays are emitted. The α rays, or more accurately the α particles consist of He atoms with a double positive charge, which are identical with He nuclei and move with $^1/_{15}$ to $^1/_{20}$ of the velocity of light. In the neutral He atom two negative electrons revolve round the positive doubly-charged nucleus. β rays are negative electrons moving with from $\frac{1}{3}$ up to almost the complete velocity of light. The γ-rays also emitted in many radioactive disintegrations are electromagnetic waves with a frequency exceeding that of X-rays.

RdAc and AcX are solid bodies, but AcEm is a rare gas which escapes from actinium preparations. The AcA arising from this is deposited upon solid objects exposed to AcEm, thus forming the first member of the "active deposit"; AcA, however, decomposes so quickly that it can only be obtained in the presence of AcEm. If, therefore, a solid object (a wire or a metal plate) is removed from the AcEm atmosphere, the active deposit consists only of the longer-lived AcB and its disintegration products, and the decomposition of these is to be studied further.

References :—

Eucken, Jette, and Lamer. §§ 269-83.
Nernst. Bk. II, Chap. XII.
G. v. Hevesy and F. Paneth. A Manual of Radioactivity, English edition, 1926.
K. Fajans. Radioactivity, English edition, 1923.
H. S. Taylor. Chap. XXI.

(b) Collecting the active deposit from AcEm

The arrangement shown in Fig. 31 is used: the actinium preparation is placed in the shallow pan S, resting on the metal plate B, which is insulated underneath. It is covered by the bell-shaped metal case G, provided with a circular opening at the top; through this is introduced a metal wire, insulated by an ebonite stopper K, and carrying at its lower end a horizontal metal plate P; this plate serves to collect the active deposit, and is 3 or 4 cm. away from the active preparation. Since the disintegration products of AcEm assume a positive charge in air, the base B and the metal cover G are connected to the $+^{ve}$ pole of the 110 or 220 volt main leads, and the metal rod and plate P to the $-^{ve}$ pole. A water-resistance W is connected in to avoid any risk of a short circuit. The disintegration products are then repelled away from the base and the cover, but attracted towards the plate. If the latter is covered with a thin foil of aluminium or tin (by cutting out a disc of rather larger radius than P and folding the overlapping part on to the back side of the plate), then the active deposit collects on the side of the foil facing the actinium preparation. It is best to expose the foil for three or four hours, after which it is carefully removed for the experiment by means of forceps. It should not be touched with the fingers, because the active deposit comes off easily.

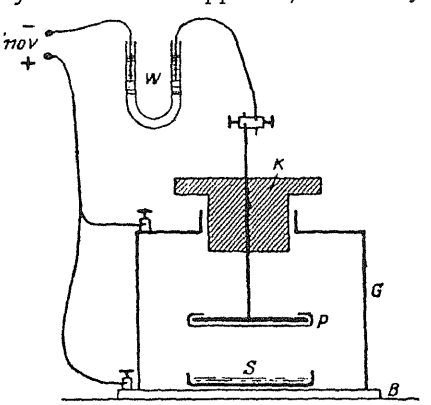

FIG. 31.—Collecting the active deposit.

(c) Decomposition of the active deposit of AcEm.

(1) Theory

AcB decomposes according to the scheme :

$$\begin{array}{ccccccc} & & & 99{\cdot}85\% & & & \\ & (\beta) & & \alpha & & & \\ \mathrm{AcB} & \longrightarrow & \mathrm{AcC} & \longrightarrow & \mathrm{AcC''} & & \\ 36{\cdot}1\ \mathrm{m} & & 2{\cdot}16\ \mathrm{m} & \searrow & 4{\cdot}76\ \mathrm{m} & \searrow \alpha & \\ & & & \beta & & & \\ & & & 0{\cdot}15\% & \mathrm{AcC'} & \longrightarrow & \mathrm{AcD\ (Actinium\ lead).} \\ & & & & 0{\cdot}005\ \mathrm{s.} & & \end{array}$$

The β-rays which are emitted directly from AcB have so little penetrating power that they cannot be detected by the measuring device used here (see Fig. 32). AcC decomposes in such a way that only 0·15 per cent. of all the atoms break up to form AcC′, the majority (99·85 per cent.) giving rise to AcC″. The β-rays produced in the formation of AcC′ are therefore so weak that they are of no importance in the present experiment. In the apparatus used (a β-ray electroscope)[1] the α-rays emitted from the AcC′ are absorbed by a sheet of aluminium leaf introduced between the preparation and the electroscope chamber. (0·06 mm. of aluminium cuts off even the fastest α-rays.) Thus only the β-rays from AcC″ are observed and measured.[2] The fact that with their help the rate of decomposition of AcB can be determined is due to the circumstance that AcC and both AcC′ and AcC″ are considerably more short-lived than AcB. So long as AcB is present as the parent substance, its disintegration products stand in the relationship of "radioactive equilibrium" with it. The simplest case of radioactive equilibrium is when a parent substance A is so long-lived in comparison with its disintegration product B that the quantity of the parent substance may be taken as constant during the experiment. (E.g. Ac and AcEm.) Starting with the pure parent substance, the product is formed in increasing amount until a limiting value is reached when the amount of B being decomposed in unit time equals the constant amount being formed from the parent substance. Then in the stationary state :

[1] The experiment can also be done in an α ray electroscope (see W. Makower and Geiger, "Practical Measurements in Radioactivity," Longmans, 1912). In this case it is mainly the α-rays from AcC which are effective.

[2] The ionising action of the γ-rays of AcC″ is so weak in comparison with that of the β-rays that it can be neglected.

$$+\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k_a[A].$$

$$-\frac{d[B]}{dt} = k_b[B].$$

$$+\frac{d[B]}{dt} = -\frac{d[B]}{dt} \text{ or } k_a[A] = k_b[B]\,;$$

$$\frac{[A]}{[B]} = \frac{k_b}{k_a} = \frac{(t_h)_a}{(t_h)_b} = K_0 \quad . \quad . \quad . \quad . \quad (36)$$

The square brackets signify amounts of the substances in question. The meaning of this is that in radioactive equilibrium the amounts of the two substances are in inverse proportion to the respective decomposition constants, and in direct proportion to the half-value times. If the parent substance is longer-lived than the product, but nevertheless decreases in amount at an appreciable rate, then the amount of B formed in unit time, and also the amount present at any time, decrease in the same proportion. Calculation shows that in this "transient" radioactive equilibrium[1] which is set up after a time, the proportion of A to B remains constant; in this case, however, we have

$$\frac{[B]}{[A]} = \frac{k_a}{k_b - k_a} \quad . \quad . \quad . \quad . \quad (37)$$

When k_a is negligible in comparison with k_b, equation (37) goes over into equation (36).

The relationship which has just been discussed applies to the case of AcB changing into AcC and also AcB into AcC″. In the latter case the intervention of AcC merely delays the attainment of equilibrium, but leaves the other conditions unaltered. Thus in equal times the quantities of AcC″ and AcB decrease in the same proportion. If, therefore, the decrease in amount of AcC″ is followed by means of the ionising action of the β-rays which it emits, this provides indirectly a measure of the rate of decomposition of AcB and hence of its disintegration constant.

(2) Experimental

(α) *Principle of the Method.*—The rate of discharge of an electroscope serves as a measure of the amount of radioactive substance present at different times, the rate being proportional

[1] As distinguished from "permanent" or "secular" equilibrium, when the parent substance is almost infinitely long-lived in comparison with the product.

to the amount. The β-rays entering the electroscope chamber produce positive and negative gas ions from the neutral N_2 and O_2 molecules of the air. A single β-particle of moderate velocity can produce in its path several thousand positive and negative gas ions. The positive ions which are formed neutralise the charge of the electroscope leaf (negatively charged by means of a rubbed ebonite rod), while the negative ions give up their charge to the earthed walls of the electroscope chamber. The more ions there are produced, the more rapidly is the leaf discharged. The number of ions depends upon the number of β-particles entering; this is determined by the number of radioactive atoms disintegrating, which in turn is proportional to the total number of radioactive atoms present, as has been shown above.

The rate of discharge is measured by allowing the electroscope leaf to fall along a scale, and determining the time required to pass over a definite number of scale divisions.

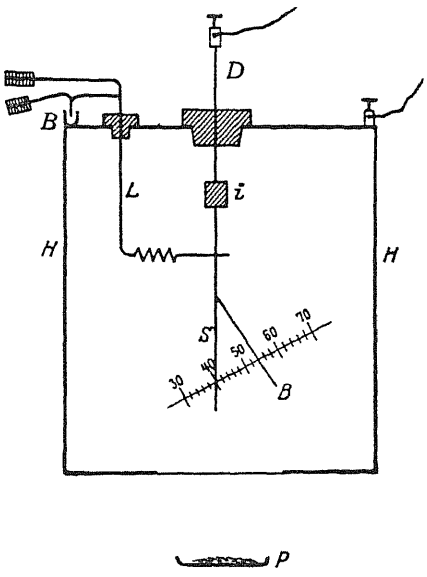

FIG. 32 —β-ray electroscope.

(β) *Charging the Electroscope.* — The essential part of the electroscope is the rod S, with the attached leaf B (Fig. 32), consisting of an extremely thin gold or aluminium strip, which becomes charged in the same sense as S, and because of the repulsion takes up an inclined position. The rod is insulated by means of the amber knob *i* from the earthed wire D, which is fastened in the centre of the cover of a cubical metal case, by means of an ebonite plug. The leaf is observed from outside through mica windows in the front and back, using a telescope magnifying ten-fold. The metal case H, and also the wire D, are earthed by being connected to the water or gas mains by soldered wire connexions. The charging up is done with the help of the "charging handle" L, which is fastened through an ebonite plug; the part inside the case is flexible. The handle

can be brought into metallic contact with the rod S, so that the charge of a rubbed ebonite rod, when stripped off on to the part of the charging handle outside the case, is transferred to the rod and the leaf. After use the charging handle is moved to a position 90° away from the charging position, and is there fixed by means of the springy wire loop soldered on, which dips into the small mercury-filled cup B; the latter being in metallic connexion with the case, the earthing of the charging handle in this position is ensured.

(γ) *Adjustment of the Scale.*—For the scale, micrometer divisions in the eye-piece of the telescope are used. The scale is given an inclination of 30° to 40° to the horizontal by turning the eye-piece, and the telescope brought into such a position that the electroscope leaf with a moderate deflection (30° to 40°) is in the field of view. The next step is to focus sharply on the front or back edge of the leaf, and observe whether this sharpness is maintained over the whole range of measurement; if not, the reason is that the telescope eye-piece scale is not accurately parallel to the plane of motion of the leaf, and this is remedied by moving the telescope or turning the electroscope stand. It is now necessary to find the position of the scale with which an equal number of scale divisions are passed over in equal intervals of time, in the middle range (divisions 20 to 70)—with a source of constant activity. The latter is best obtained by using the black oxide U_3O_8 (mean life of Uranium $6{\cdot}4 \times 10^9$ years) which is placed in a shallow pan on the support P beneath the electroscope case. The strength of the preparation, i.e. the quantity of uranium oxide, is arranged to be such that for ten scale divisions fifteen to twenty seconds are required. The electroscope is charged; at the moment when the selected edge of the leaf passes division 70 (or the point of intersection of this division with the line drawn across the whole scale—this form of scale (see Fig. 32) is much more conveniently and accurately read than the ordinary form without any horizontal line) the stop-watch is started, and stopped again on passing division 60. The time interval is noted, and a similar measurement made between 50 and 40 and finally between 30 and 20. After charging up again the time intervals are measured between 60 and 50 and between 40 and 30. Since the position of the leaf at each scale division can be read with an accuracy of about 0·1 division, there is an error of 2 per cent. over the ten scale divisions. If instead of merely the irregular fluctuations in the time values caused in this way, there is a regular "drift," then the scale is set somewhat more steeply,

and the measurements repeated. If now the drift is less, but not quite removed, a still steeper setting is tried; if on the other hand it is greater, a less steep setting is required.

An exact record of the whole series of trials is kept, noting each time the sense in which the position of the scale has been altered with respect to the preceding trial. After three or four changes it is easy to find a position in which there is no longer any appreciable drift. *This position must be kept unchanged throughout the whole experiment.* If an irregular "jerk" of the leaf occurs at any place on the scale, the microscope must be moved and another region found.

(δ) *Determination of the Natural Leak.*—By this is meant the spontaneous discharge of the electroscope caused by the normal content of ions in the air and by incomplete insulation of the electroscope leaf. It is expressed in scale divisions per minute. It is determined by charging the electroscope after removal of the uranium preparation, and measuring with a stop-watch the time required for the leaf to pass over ten scale divisions. The leak calculated from this should not exceed one scale division/min.; otherwise there is some defect in the insulation, or the electroscope is radioactively infected.

(ε) *Measurement of the Decomposition of* AcB.—The Al- or Sn-foil is carefully removed with forceps from the collecting-plate of the apparatus in which the active preparation is obtained (Fig. 31), and laid with the active surface upwards in a shallow dish on the stand of the electroscope which carries the preparation. After about $\frac{1}{4}$ hour the measurement is begun. If the initial activity exceeds 100 scale divisions/min. the preparation is divided by cutting the Al-foil. Because of the large rate of discharge, a range of fifty divisions of the scale is first chosen. It is important to consider here the accuracy of the measurement: the stop-watch can be read to $\frac{1}{5}$ second. To obtain an accuracy of 1 per cent. in the time measurement, the duration of the observation must be at least twenty seconds. In proportion to the gradual decrease in the rate of fall, a smaller number of scale-divisions can be selected, so that the individual measurements last for two to three minutes. The experiment is terminated when ten scale divisions require more than two to three minutes.

An exact record of the measurements is kept, noting the *absolute time* of the beginning of each measurement to the nearest five seconds, the *scale range* over which it is made, and the *time determined by the stop-watch* taken by the leaf in moving over the range in question. In the first hour measurements are

made every ten minutes, in the second every twenty minutes, and in the third every half-hour. After three hours the preparation is almost inactive. After finishing the measurement the natural leak is determined again.

(ζ) *Calculation of the Results.*—First the activity of the preparation is calculated for each measurement, and expressed as rate of fall in scale divisions per minute. For example, if fifty scale divisions are passed over in 70·6 seconds, the activity is $\frac{50 \times 60}{70 \cdot 6} = 42 \cdot 5$ scale divisions/min. The natural leak must be subtracted from the activity found in this way. The absolute time t to which this corrected activity refers is not the time of the beginning of the measurement in question, as recorded, but the "mean time of the observation" = initial time + $\frac{1}{2} \times$ the duration of the observation. If, for example, a measurement is commenced at 2 hrs. 25 mins. 20 secs., and 70·6 seconds was required for fifty scale divisions, then with a natural leak of 0·7 scale divisions per minute, the value to be taken in the calculation is a corrected activity of $42 \cdot 5 - 0 \cdot 7 = 41 \cdot 8$ at 2 hrs. 25 mins. 55·3 secs. This procedure of taking a mean activity at a mean time is not entirely correct, since the radioactive decomposition follows a logarithmic and not a linear law. If, however, the duration of a measurement is small ($< \frac{1}{6}$) in comparison with the half-value period, then the error caused in this way ($<$ 0·2 per cent.) is within the experimental error arising in other ways.

The decomposition constant k is calculated according to equation (33), putting for the number of radioactive atoms the activity, to which the number of atoms is proportional. t_1 and t_2 are the mean observation times.

The separate measurements are combined so that different measurements are taken in pairs, always in such a way that the time interval between them is as large as possible (for the sake of the relative accuracy of $t_2 - t_1$). Thus if twelve measurements have been made in all, 1 is combined with 7, 2 with 8, and so on, finally 6 with 12. The mean of the values obtained is taken.

The reciprocal of the decomposition constant k is called the "mean life":

$$t_m = \frac{1}{k} \quad . \quad . \quad . \quad . \quad (38)$$

The meaning of this magnitude may be pictured as follows: if by replacing the decomposing atoms the number of radio-

active atoms is kept constant—as is the case with a short-lived radioactive element in the presence of its long-lived parent substance—then the mean life is the time required for as many atoms to decompose as were present originally (and present, therefore, during the whole period).

(η) *Graphical Representation of the Results.*—By plotting as abscissæ in a co-ordinate system the "mean absolute time" of the separate observations and the corresponding corrected activities as ordinates, a logarithmic curve is obtained (see p. 103). If, instead, the logarithms of the corrected activities are plotted, the points obtained must lie approximately upon a straight line (see p. 103). It is convenient for this purpose to make use of "logarithmic" paper, having a logarithmic graduation along one co-ordinate axis, and ordinary mm. divisions along the other. The logarithmic graduation is so arranged that corresponding to each number written at the side a distance proportional to the logarithm is marked off. (Compare the slide-rule.) Then, without looking up the logarithms, the values of the corrected activities can be plotted on the logarithmic graduation, and the mean times of the experiments on the mm. graduation. According to the ratio of the largest and smallest activities to be plotted, the logarithmic paper is chosen to cover one (1 : 10) or two (1 : 100) powers of ten. If, although having a ratio smaller than 10 : 1, the values to be plotted fall into different powers of ten (e.g. 45 : 5), and if the logarithmic graduation covers only one power of ten, then all the values must be divided by some one number, chosen sufficiently large to make all the quotients fall under one power of ten.

By finding, on the straight line obtained in this way, two values of the activity which are in the ratio of 2 : 1, then the difference between the corresponding absolute times gives directly the half-value period, although less accurately (by this simple method) than the exact calculation according to formula (33) or (34). The correct numerical value of k can be taken as directly equal to the tangent of angle of slope of the straight line only if in the plot the distance chosen to represent the unit of time is the same as the distance representing the logarithmic unit multiplied by 0·4343. If $\log_{10} 10 = 1$ dm., then one minute must be taken as = 0·4343 dm.

XI. VELOCITY OF CHEMICAL REACTIONS

A. INVERSION OF CANE-SUGAR

(a) Theory

THE hydrolysis of cane-sugar takes place according to the equation

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

The velocity of this reaction is very strongly accelerated by $H^{\cdot}$-ions. Under the experimental conditions employed the relative molar quantities of water and sugar are about 85 : 1. The reaction proceeds, therefore, as though it were unimolecular, for the reasons already discussed on page 104. The hydrolysis is followed in a polarimeter, the change in cane-sugar concentration being determined by measuring the change in the angle of rotation of the reaction liquid, to which it is proportional. A solution of pure cane-sugar is dextro-rotatory. The mixture of glucose and fructose produced by the fission is lævo-rotatory since fructose rotates to the left more strongly than glucose to the right. As the hydrolysis proceeds, i.e. with decreasing concentration of cane-sugar, the original dextro-rotation gradually becomes smaller and smaller, finally changing over to lævo-rotation. To the complete disappearance of cane-sugar corresponds the total change of the angle of rotation $\alpha_i - (-\alpha_f)$; (the final angle $-\alpha_f$ is taken as negative since it corresponds to a lævo-rotation). Thus $\alpha_i - (-\alpha_f)$ is a measure of the total amount of cane-sugar originally present. Similarly, at any time t the angle read, diminished by the value of the negative final angle, is a measure of the amount of cane-sugar remaining at this time: $\alpha_t - (-\alpha_f) \sim c_t$. Therefore, in equation (33) in place of the number of molecules the differences (rotation angle — negative final angle) which correspond to cane-sugar concentrations, can be introduced:

$$\frac{\log_{10}[\alpha_{t_1} - (-\alpha_f)] - \log_{10}[\alpha_{t_2} - (-\alpha_f)]}{0{\cdot}4343\,(t_2 - t_1)} = k \quad . \quad (39)$$

(b) Experimental

(1) *Preparation and Temperature Control of the Solutions.*—20 gms. of loaf-sugar are dissolved in a measuring flask and the volume made up to 100 c.c. with distilled water. The solution is filtered into a conical flask and sterilised with a particle of thymol or camphor; it is then placed in a 25° thermostat, weighted down by a lead weight. At the same time a 100 c.c. conical flask containing 40 c.c. $\frac{N}{1}$ HCl and another containing 40 c.c. $\frac{N}{2}$ HCl are put into the same thermostat, to warm up. All three solutions must remain for fifteen to thirty minutes in the thermostat before they can be used.

(2) *Apparatus.*—Two polarimeter tubes are carefully cleaned inside with distilled water; after filling one of them with distilled water the adjustment of the polarisation apparatus is practised. A Lippich half-shadow instrument is used; in this a parallel monochromatic beam of light, after leaving the polarising Nicol prism, is divided into two parts with somewhat different directions of vibration, by means of a small auxiliary Nicol. The auxiliary Nicol is introduced into one part of the path of the rays, and is so set by means of a lever that its plane of vibration is rotated through a small angle with respect to the plane of vibration of the polarising Nicol. (This setting of the auxiliary Nicol must not be altered during any one series of measurements.) Thus on looking through the analyser, with crossed Nicols only one-half of the field of view appears completely dark. If now the analyser is turned so that its plane of vibration is exactly perpendicular to the bisecting line between the vibration planes of the polariser and the auxiliary Nicol, both halves of the field of view appear equally bright. A small alteration of this position makes one-half darker and the other brighter, and it is possible, with practice, to reproduce the setting at which the half-shadow just disappears to within 2 to 3′. An electric lamp in front of which is an accumulator trough filled with concentrated potassium dichromate solution serves as a source of light; the light is then sufficiently nearly monochromatic. After putting in the polarimeter tube filled with water, the eye-piece is focussed sharply on the line of separation between the two halves of the field of view, which differ in colour and brightness. Then by turning the vertical screw situated under the divided circle the position is found in which the two halves of the field appear as much alike as possible.

Degrees and half-degrees are read on the divided circle, and with the help of the vernier single minutes can be determined. This should be practised until the setting can be reproduced accurately to one or two minutes.

Even during these preliminary exercises the two polarimeter tubes are connected by rubber tubing to the circulating pump which pumps water out of the thermostat through the outer metal jacketing tube surrounding the actual glass polarimeter tube and making it possible to keep a constant temperature inside. Naturally the temperature of the thermostat water is altered to some extent by streaming through the rather long leads. If the room temperature remains the same a constant difference between the temperature of the thermostat and that of the contents of the polarimeter tube, which is easily measured (and tested for constancy) by a thermometer dipped into the opening in the polarimeter tube which serves for filling.[1]

(3) *Carrying out the Measurement.*—After the solutions have been warmed for a sufficient length of time, 40 c.c. of cane-sugar solution is added to 40 c.c. of $\frac{N}{1}$ HCl, and also to the same amount of $\frac{N}{2}$ HCl. Thorough mixing is ensured by shaking round. The distilled water is now shaken out of the polarimeter tubes, each washed out three or four times with one of the sugar solutions, and finally filled with the proper solution. The solutions are allowed to flow in slowly, since otherwise air bubbles are apt to be carried in. In this case the field of view is either indistinct and clouded all over, or else the upper half is irregularly darkened. Such air bubbles are removed by inclining the tube and at the same time gently tapping it; sometimes it has to be emptied and refilled. From this point onwards care is taken to keep the thermostat at as constant a temperature as possible (see pp. 3 and 119).

About $\frac{1}{4}$ hour after filling the tubes measurements are begun, a reading of each tube being taken every twenty minutes—alternately for convenience, the readings of one tube being then displaced by ten minutes with respect to the other. The absolute time of the reading, the angle of rotation, and the thermostat or tube temperature are tabulated. Three readings are always taken in quick succession, and the mean of the three

[1] The polarimeter tube can also be surrounded by a glass, water-filled jacketing tube, and completely immersed in the thermostat between measurements. It is taken out and dried for a measurement. If the jacketing tube is large enough the temperature remains satisfactorily constant during a measurement.

taken at the mean time of the observation. Only in this way can sufficient accuracy be obtained in the early stages, since the angle changes very quickly, especially in the tube with the stronger acid; but it is advisable to follow this procedure in the later stages as well, when the alteration takes place more slowly. In the second to the fourth hours it is sufficient to take readings every half-hour, and from then on, every hour. If the experiment is begun in the morning, the final angle for the solution with the stronger acid can be read in the evening of the following day, and with the weaker acid, on the morning of the third day. With the acid concentrations used, the concentration of cane-sugar after the times mentioned will have fallen to less than 1 per cent. of its initial value.[1]

(4) *Calculation of the Results.*—Both sets of results are calculated by means of formula (39). For the method of combining the individual measurements, see page 112. From the individual values of k the mean is calculated, and by formula (2) page 6, the mean error of the mean. The results are also plotted graphically on ordinary mm. squared paper, and upon logarithmic co-ordinate paper (see p. 113). In the latter case the angle $\alpha_t - (-\alpha_f)$ is plotted on the logarithmic ordinate-axis, the absolute time values on the abscissa-axis, divided in mm.

It will be found that the rate of inversion in the solution containing $\frac{N}{1}$ acid is about twice as great as in the solution with $\frac{N}{2}$ acid. The catalytic acceleration of the reaction by the $H^{\bullet}$-ion is therefore approximately proportional to its concentration, or more accurately, to its activity. Hence the measurement of the rate of inversion of cane-sugar can be used to determine $H^{\bullet}$-ion concentration (cf. p. 65). After the experiment both tubes must be emptied and thoroughly washed out with distilled water.

B. HYDROLYSIS OF METHYL ACETATE

(a) Theory

The hydrolytic decomposition of methyl acetate into acetic acid and methyl alcohol under the catalytic influence of two

[1] The end-point of the reaction can be approximately calculated beforehand, when the angle is no longer altering much, i.e. the reaction is nearly over, by determining from the readings the approximate value of the half-value period. It is easily shown that after seven times the half-value period calculated from the beginning of the experiment, the concentration will have sunk to less than 1 per cent. of its initial value, and after ten times, to less than 0·1 per cent. of the initial value.

different $H^{\cdot}$ ion concentrations is measured at 25°. Because of the great excess of water (with the quantities given the molar ratio of water to ester is 74 : 1) the reaction proceeds as a unimolecular reaction (cf. p. 104). The concentration of methyl acetate remaining at various times is determined by titration of 2 c.c. of the reaction mixture with baryta solution. If at time t n_t c.c. of $\frac{N}{10}$ $Ba(OH)_2$, and after complete hydrolysis n_f c.c. of the alkali are required, then $n_f - n_t$ corresponds to the extra amount of acid, which in 2 c.c. of the reaction mixture between time t and the end of the reaction, is produced by hydrolysis. But this quantity of acid is equivalent to the amount of ester still remaining at time t, from which it is formed.

The added catalytic acid is of course titrated as well; but its amount remains unaltered.

(b) Experimental

(1) *Procedure.*—Conical flasks to contain the two reaction mixtures are repeatedly washed out with distilled water, steamed out for ten minutes, and dried in the oven. 40 c.c. $\frac{N}{1}$ HCl is placed in one, and 40 c.c. of $\frac{N}{2}$ HCl in the other; they are then weighted with lead weights and closed with paraffined corks, and placed in the 25° thermostat. After about half an hour 2 c.c. of methyl acetate is added to each of the quantities of acid, well mixed by shaking round, and left for at least fifteen minutes in the thermostat. For the titrations 2 c.c. of the reaction mixture is removed with a 2 c.c. pipette and titrated with $\frac{N}{20}$ alkali. If only $\frac{N}{10}$ alkali is available, 4 c.c. of reaction mixture must be taken each time, so that the amount of alkali used and hence the accuracy of the titration is not too small. The titrations are done in 100 c.c. conical flasks, with the addition of two or three drops of phenolphthalein as indicator. Before each titration 20 c.c. of ice-cold distilled water is placed in the flask to be used, and the 2 or 4 c.c. of reaction mixture added to this. The strong cooling practically brings the hydrolysis to a standstill. Hence the absolute time to which the acid or ester concentration is to be referred is the moment at which the reaction mixture flows into the ice-water. The titrated mixture is thrown away, the flask washed again with distilled water, and kept ready for the next determination.

During four hours one titration of each reaction mixture is done every half-hour; alternately for convenience, so that the determinations belonging to one series are displaced by a quarter of an hour with respect to the other. In each case portions are preserved for the determination of the final titre. If the experiment is begun in the morning, the end-point is determined for the mixture with $\frac{N}{1}$ HCl on the evening of the next day, and for the $\frac{N}{2}$ HCl mixture, on the morning of the third day. In this time, with the acid concentrations used and the temperature specified, the ester concentration will have fallen to less than 1 per cent. of its initial value (cf. p. 117). During the whole experiment care must be taken that the temperature is kept exactly constant. For both series a table is made of the following data: the absolute time at which the sample is run into the ice-water, the number of c.c. of alkali used, and the thermostat temperature. Since only relative values are dealt with in the whole determination, the titre of the alkali used need not be known; it is only necessary that for all determinations the same alkali be used.

(2) *Calculation of the Results.*—This is done according to the formula

$$\frac{\log_{10}(n_f - n_{t_1}) - \log_{10}(n_f - n_{t_2})}{0{\cdot}4343\,(t_2 - t_1)} = k \quad . \quad . \quad (40)$$

For further details, see page 112 (Radioactivity) and page 117 (Inversion of Sugar). Here also, as with the cane-sugar inversion, the reaction velocity in the presence of $\frac{N}{1}$ acid is approximately twice as great as in the case of $\frac{N}{2}$ acid, so that there is approximate proportionality between hydrogen ion concentration and reaction rate (cf. p. 65).

(3) *Appendix: Thermostats and Thermoregulators.*—To maintain a temperature constant to within a few hundredths of a degree in the range from 0° to the region of 100° C., the most suitable means is a water thermostat with a thermoregulator. (Above 70° the water should be covered with a layer of oil.) It consists of a large water container, in which the temperature is kept very uniform by vigorous stirring. The thermoregulator automatically switches on and off a heating arrangement. The construction and action of the usual type of thermoregulator for electric heating is shown in Fig. 33. The cylindrical container

T contains toluene. (For temperatures below 40° chloroform may be used with advantage, which has a somewhat greater coefficient of expansion, and contaminates the mercury less.) As the toluene expands with rising temperature, it pushes back the confining liquid (mercury) a little and the mercury column rises slightly. As a result, in the capillary to which the vertical tube is joined, contact is made at the point K between the top of the mercury column and the platinum wire P, which is sealed through the lower end of the small tube A (filled with mercury) and to which one pole of an accumulator B is connected; as an alternative to using an accumulator a small potential difference may be tapped off from the mains by means of a suitable resistance lamp. (With too large a voltage strong sparking occurs at the contact, and the mercury surface is soon contaminated by oxide formation.) The other pole of B is connected to the windings of the electromagnet M and is in metallic connexion, through the side tube Z filled with mercury and the fused-in platinum wire O, with the mercury column of the regulator. When contact is made at K this circuit is closed; the electromagnet M attracts the little iron plate E at one end of the lever H, so that the iron point at the other end of the lever is drawn out of the mercury cup N. This breaks the circuit which includes the main leads and the heating lamp L in the thermostat. The lamp goes out; the thermostat cools, the toluene in the regulator contracts and the contact at K is broken. M then loses its attracting force; the small plate E becomes free and the iron point dips into N again, and the circuit of the heating lamp is made again. By screwing in and out the screw S the position of the mercury in the capillary can be regulated. The fine adjustment to the desired thermostat temperature is done in this way, while the rough setting is given by the total amount of mercury in the column. C is a

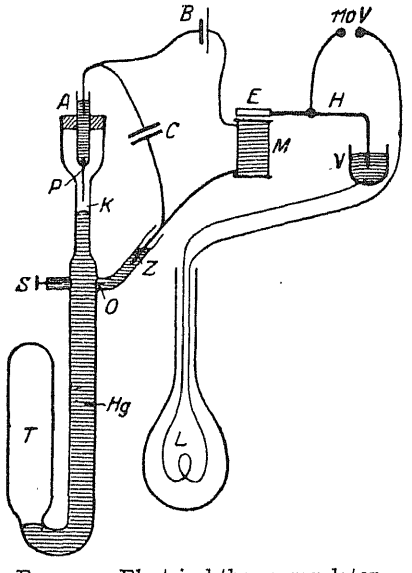

FIG. 33.—Electrical thermoregulator.

condenser of 1 MF connected in parallel across the contact K to prevent sparking and thus diminish contamination of the mercury meniscus. With the construction described, the temperature can be kept constant to within $^1/_{30}$° to $^1/_{100}$° C., according to the size of the toluene vessel (what is important is the size of its *surface* rather than its *volume*), the fineness of the capillary and the intensity of the stirring.

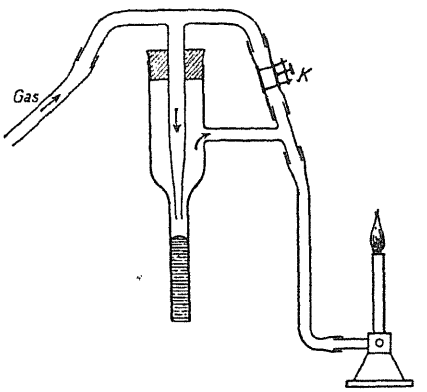

FIG. 34.—Gas thermoregulator.

With thermoregulators for gas heating (Fig. 34 shows only the top of the regulating arrangement) the rise or fall of the mercury in the capillary interrupts or gives free passage to the gas stream to the burner, whereby the actual height of the heating flame is regulated. Through the other arm of the leads a "pilot" flame is maintained at which the heating flame is always relit, and which is of such a size (regulated by the screw-clip K) that by itself it does not keep up the temperature of the thermostat, but allows it to sink slowly.

References :—
Ostwald-Luther, p. 106 *seq.*
Reilly, Rae, and Wheeler. Chap. IX.

XII. OPTICAL MEASUREMENTS

REFRACTOMETRY

(a) Theory

(1) *Polarisation.*—According to modern views all substances, in the last analysis the atoms, are composed of positive and negative electric charges. The arrangement of these charges inside a neutral molecule differs from case to case. The distinction between molecules with and without a dipole moment is of importance. In the latter class, e.g. CCl_4, C_6H_6, the electrical centres of gravity of the positive and negative charges coincide; thus even at relatively small distances (of the order of magnitude of a molecular diameter) they exert no electrical

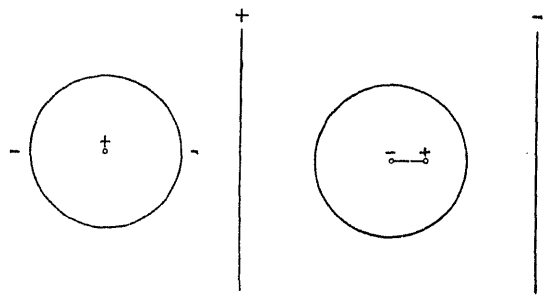

FIG. 35.—Polarisation of an atom in an electric field.

force outside. With molecules having a dipole moment (P. Debye), e.g. HCl, CH_3OH, $C_6H_5NO_2$, these centres of gravity lie at different places in the molecules. Such molecules have a positive and a negative end, a + and a — pole.

Under the action of an external electric field the two kinds of molecules behave differently. If molecules which have no dipole moment are brought into the field, e.g. between the plates of a charged condenser, then because the electric charges inside the molecule are not quite rigidly bound together, the positive charges are displaced towards the negative plate of the con-

denser and the negative charges in the opposite direction (Fig. 35 illustrates the case of a monatomic molecule). The originally coincident centres of gravity of positive and negative charges now separate; a dipole is formed. The stronger the electric field and the looser the binding between the charges, the greater will be the relative shift, or the deformation of the molecule (the deformation part of the polarisation). The extent of the deformation will be measured by the magnitude of the induced dipole moment m. This is equal to the product of the charge E considered as situated at each of the centres of gravity, and the distance l separating the centres of gravity, so that $m = E \cdot l$.

With a substance, the molecules of which already have a dipole nature, the action of the electric field is somewhat different, in so far as here besides the shift of the charges, a further effect is produced, namely the spatial orientation of the existing dipoles (orientation part of the polarisation). In the absence of an electric field the dipoles are oriented in all directions on account of the thermal agitation. But when the field is applied the positive ends of the dipoles are attracted towards the negative plate and repelled from the positive, while the negative ends are affected in the opposite sense. Hence the dipoles are turned and directed by the electric field, and the more strongly the stronger the electric field and the larger the dipole moment, on the one hand, and the lower the temperature on the other hand.

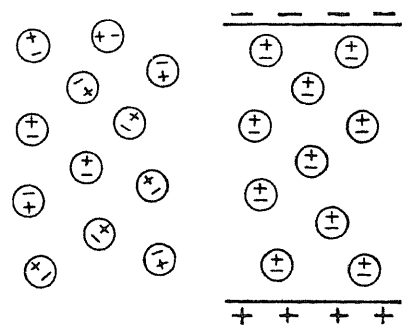

FIG. 36.—Orientation polarisation.

Fig. 36 shows the limiting case for so low a temperature or so high a field strength that the thermal effect no longer plays any part in comparison with the orientation effect. The total effect of the formation of dipoles by deformation and the orientation of previously existing dipoles is called "*polarisation.*"

(2) The polarisation is intimately connected with the *dielectric constant* ϵ. By the dielectric constant is meant the proportion in which the force E_0 emanating from a charge in a vacuum is weakened by the dielectric: $\epsilon = \frac{E_0}{E}$. The dielectric constant of a vacuum is therefore 1. The connexion between the

dielectric constant and polarisation (natural or induced dipoles) can be seen from Fig. 37. Suppose that between the plates of a charged condenser there are oriented molecules carrying dipoles, then the action of the positive charges of the lowest layer of molecules can be imagined to be compensated by the negative charges of the second layer, and so on as far as the positive charges of the last but one layer of molecules, which are compensated by the negative charge of the uppermost layer. There remain over, therefore, a negative layer next to the positive plate and a positive layer next the negative plate, the effect of which is to weaken the electric field action of the plates. Since the vacuum contains no molecules, it is not polarisable, so that the quantity $\epsilon - 1$ serves as a measure of the polarisability of a dielectric medium (for the vacuum $= 0$; $\epsilon = 1$).

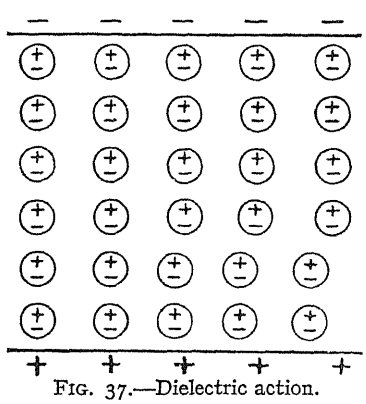

FIG. 37.—Dielectric action.

If the number of molecules in unit volume is increased then both the effects described above are increased, since there are now more particles to be deformed or oriented; if the molecules exerted no reciprocal action upon each other, $\epsilon - 1$ would increase in proportion to the density. But a molecule will be deformed and oriented by neighbouring molecules as well as by the action of the electric field—and, as Fig. 37 shows, in the sense that the action of the applied field is increased, whence it comes about that it is not $\epsilon - 1$, but a more complicated expression $\frac{\epsilon - 1}{\epsilon + 2}$ (according to Clausius and Mosotti) which is proportional to the density, to a first approximation. Thus on dividing by the density one obtains a quantity characteristic of a particular substance, the "*specific polarisation*" p:

$$p = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} \quad . \quad . \quad . \quad . \quad (41)$$

Multiplying by the molecular weight gives the expression $P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$, the "*molecular polarisation*" (Debye, Ebert),

which in complex systems can be calculated additively from the individual constituents (although not in all cases).

(3) The passage of electromagnetic waves, whether Hertzian or light waves, through a body affects the molecules, through the alternating electric field, in a similar way to a static electric field. Here the effect shows itself in a slowing up of the propagation of the waves. (This point cannot be gone into more fully here.) The expression $n - 1 = \frac{c_0 - c}{c}$ provides a measure of the relative lowering of velocity; (n is the refractive index, which expresses how many times the light velocity c in the medium in question is smaller than the velocity c_0 in a vacuum; thus $n = 1{\cdot}5$ means that the velocity in the medium is $\frac{300000}{1{\cdot}5}$ km./sec.). For electromagnetic waves of relatively large wave-length (small frequency) the relationship $n^2 = \epsilon$ holds, according to Maxwell, so that the determination of the velocity of propagation of Hertzian waves in a medium serves to measure its dielectric constant ϵ. (The wave method of Drude and Lecher.) The action of light waves upon the molecules differs from that of a static field or of Hertzian waves in that in this case the dipoles carried by the molecules do not follow the changes of direction of the electric alternating field, which takes place with a very high frequency, so that for the interaction of light waves and molecules, and therefore also for the quantity $n - 1$, an orientation effect does not arise, and it is practically only the deformation part of the polarisation which plays any part.

The further considerations which follow are concerned exclusively with light waves. For the same reasons as were given above for $\epsilon - 1$, the expression $n - 1$ is also not simply proportional to the density, but increases more rapidly than this. Proportionality with the density exists, however, for the expression $\frac{n^2 - 1}{n^2 + 2}$, which is formed quite analogously with the expression $\frac{\epsilon - 1}{\epsilon + 2}$ given above for the polarisation. Dividing by the density d, one arrives at the expression deduced by H. A. Lorentz and L. Lorenz for the "*specific refraction*" r:

$$\text{spec. refraction } r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \cdot \quad . \quad . \quad (42)$$

By multiplication by the molecular weight M the "molecular refraction" R is obtained:

$$\text{Mol. refraction } R = M \cdot r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \cdot \quad . \quad (43)$$

These expressions are found to be characteristic quantities for every substance. Their additivity in complex systems and independence of temperature and state of aggregation are often better fulfilled than in the case of molecular polarisation. This arises in part from the fact that included in the latter quantity are orientation effects from the previously existing dipoles, which unlike the deformation effect, depend upon temperature (cf. 1).

The dimensions of molecular refraction are (as may easily be seen, since n is a pure number) $\frac{\text{gm.}}{\text{gm./c.c.}} = \text{c.c.}$, i.e. a volume, and capable therefore of expression in c.c. For this reason an older view was that molecular refraction represented the true volume of the molecules, as opposed to the space which they occupied. (The molecular volume of solid sodium chloride, e.g. is 27·0 c.c.; its molecular refraction 8·52 c.c.)

The molecular refraction—strictly speaking, when extrapolated to infinitely long waves—can, with simple molecules or ions, serve as a measure of their deformability, since through the following relationship

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \frac{4}{3} \cdot \pi \cdot N \cdot \alpha \quad . \quad . \quad (44)$$

where N is the Avogadro number, the molecular refraction is related to the deformability α of the molecules, which in turn is defined by the equation

$$m = \alpha \cdot E \quad . \quad . \quad . \quad . \quad (45)$$

where m is the electric moment induced by the electric field E (cf. p. 124).

(4) The molecular refraction of organic compounds is usually divided up into values which are attributed to the individual atoms and bonds. The most important atom and bond equivalents are those for the atoms of carbon, hydrogen, and the halogens, for the oxygen atom according to its mode of combination (hydroxyl, ether, carbonyl), and similarly for the nitrogen atom (primary, secondary, tertiary amines). In addition, special increments were used for the double and triple

carbon linkage. The importance of molecular refraction for the elucidation of the constitution of organic compounds depends upon the possibility of thus dividing up the molecular refraction into atomic refractions. From the theoretical point of view it is more rational, as recent investigations have shown, not to divide it up into parts associated with atoms, but with electron groups. In this way relationships are obtained between the values for the different electronic configurations.

The refraction of light depends upon the wave-length used (dispersion). Correspondingly, the molecular and atomic refractions also depend upon the wave-length. Accordingly the tables of atomic refraction (e.g. Landolt-Börnstein) give values for the most commonly used wave-lengths.

(5) The refraction R_s of a solution which contains 1 mol (mol. wt. = M) of a strong electrolyte in G_w gm. of water can be considered as additively composed of the partial refractions of its constituents. Calling r_w the specific refraction of water, r_s that of the solution, and R_d the molecular refraction of the salt in the dissolved state, then

$$r_s\,(G_w + M) = r_w \,.\, G_w + R_d\,;$$

$$\frac{n_s^2 - 1}{n_s^2 + 2} \cdot \frac{G_w + M}{d_s} = \frac{n_w^2 - 1}{n_w^2 + 2} \cdot \frac{G_w}{d_w} + R_d \qquad . \quad (46)$$

R_d can be calculated from the experimental data n_s, n_w, d_s, d_w.

With strong electrolytes, i.e. those which are largely dissociated even at high concentrations, the quantity R_d is only slightly (although perceptibly) dependent upon the concentration, and can be additively calculated from the partial quantities of the dissolved ions (strictly speaking, only at infinite dilution). Values of the refraction of 1 mol of some ions dissolved in water, for the D line are:

Na^+	K^+	NH_4^+	Ca^{++}	Sr^{++}	Ba^{++}	Zn^{++}	Cd^{++}
0·20	2·23	4·28	0·68	1·70	4·28	0·29	2·44
Cl^-	Br^-	I^-	NO_3^-	ClO_3^-	CH_3COO^-	CO_3^{--}	SO_4^{--}
9·07	12·67	19·24	11·01	12·85	14·45	12·27	14·84

The mol refractions for the dissolved salts obtained from these values agree approximately in many cases with the value of the refraction for the solid salts, given by the formula

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}.$$

Nevertheless, there are considerable deviations: for NaI, e.g. $R_d = 19{\cdot}44$ while $R = 17{\cdot}07$. Although the majority of salts

traversing the prism on its way out into the air. The angle of emergence can be accurately measured by means of the telescope and divided circle. From what has been said, the refractive index of the prism must be greater than that of the liquid.

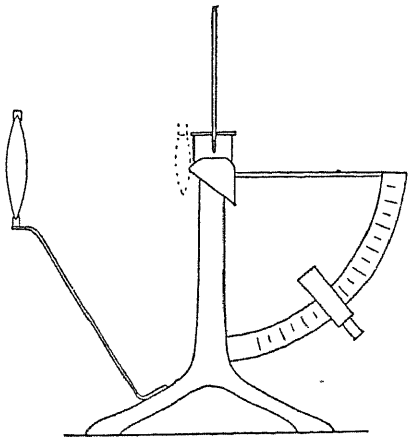

FIG. 38.

(2) *The Path of the Rays* (Fig. 39). — The bundle of rays coming from the condensing lens can introduce into the prism only rays which have an angle of refraction in the prism smaller than or equal to the limiting angle of total reflection r. To the angle r corresponds the angle of emergence e. Rays which fall below the line a are absorbed by the roughening and blackening of the conically ground upper edge of the prism. The angle e is found by setting the cross-wires of the telescope upon the sharp boundary between the dark upper part and the bright lower part of the field of view.

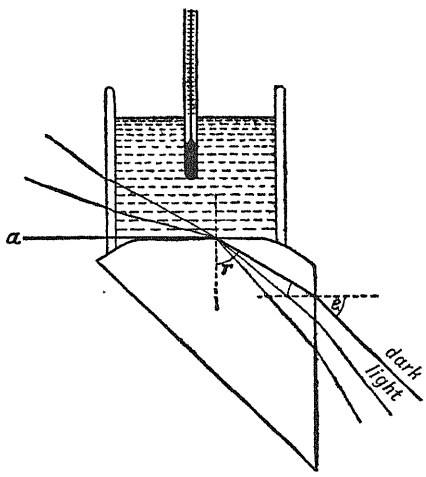

FIG. 39.

The following considerations show the relationship between the refractive index of the liquid in the cylinder, and the measured angle e:

If a is the last ray which is able to pass from the liquid into the prism, then for this ray

$$n\,(\text{liquid/glass}) = \frac{\sin 90^\circ}{\sin r} = \frac{1}{\sin r} = \frac{1}{\sqrt{1 - \cos^2 r}} = \frac{n\,(\text{air/glass})}{n\,(\text{air/liquid})}.$$

$$n\,(\text{air/glass}) = \frac{\sin e}{\sin (90 - r)} = \frac{\sin e}{\cos r}.$$

$$\cos r = \frac{\sin e}{n\ (\text{air/glass})}$$

$$\frac{n\ (\text{air/glass})}{n\ (\text{air/liquid})} = \frac{1}{\sqrt{1 - \dfrac{\sin^2 e}{n^2\ (\text{air/glass})}}}$$

$$= \frac{1}{\sqrt{\dfrac{n^2\ (\text{air/glass}) - \sin^2 e}{n^2\ (\text{air/glass})}}}$$

$$n\ (\text{air/liquid}) = \sqrt{n^2\ (\text{air/glass}) - \sin^2 e} \qquad . \quad (48)$$

For the calculation, it is therefore necessary to know the refractive index of the glass of the prism. The larger instruments are always provided with several interchangeable prisms of different kinds of glass having different refractive powers, for each of which there is a definite region of measurement. To simplify the calculation, every Pulfrich instrument has with it tables, from which the refractive index of the liquid is read directly, for the prism in question and for different angles *e*.

(3) *Manipulation of the Refractometer.*—The yellow sodium flame is used as a source of illumination. This is obtained by cutting out a semi-circular edge to a piece of asbestos paper, and putting on it a cake of sodium chloride and water-glass, made in such proportions that it is a sticky plastic mass. The prepared edge is pushed 2 or 3 mm. into the lower part of non-luminous Bunsen flame about 10 cm. in height. In this way a wide, intense Na-flame is obtained. Behind the flame is placed a large black shade, to prevent white light from the side entering with the yellow light. The measurement can be made quite conveniently in an undarkened room. The refractometer is placed about 50 cm. from the Na-flame, with the condensing lens turned towards it. The proper position is found by arranging that a sharp, inverted image of the Na-flame is formed on a sheet of white paper held on the outside of the cylinder, on the side towards the condensing lens.

From the path of the ray illustrated in Fig. 39 it is easily seen that it is sufficient that the bottom of the vessel should be covered with the liquid to be measured. It should, however, be filled to such a height that the bulb of a thermometer used to measure the temperature is completely immersed. (If the small glass cylinder becomes loose, it is fastened on again, after carefully cleaning the surface of the prism and the lower edge

of the cylinder, by coating this edge with a thin layer of secotine or some suitable cement, and applying gentle pressure to the prism. It is left for twelve hours to dry, weighting it down with a 100 gms. weight.)

The reading telescope is first placed horizontally, so that the Na-flame, the condensing lens, the upper surface of the prism and the telescope are all in one straight line. On looking through the whole field of view appears bright. The telescope is now turned slowly downwards. A dark region is seen first, and then on moving it further a sharp boundary is suddenly seen, between the upper dark region and the intense yellow part beneath. On turning further a very indistinct boundary is passed through (caused by light reflected from the upper surface of the liquid) into another dark region. The correct setting is when the cross-wires of the telescope intersect this sharp boundary (dark above, bright below). With the simple type of instrument, the telescope is arrested in this position by tightening the large screw, by means of which the divided circle, which is rigidly attached to the telescope, can be firmly clamped at the bottom, in front; the fine adjustment is made by turning the micrometer screw, which is situated below and on the left of the large screw, and moves in a direction perpendicular to the axis of rotation of the latter. (These details are omitted from Fig. 38.) On the divided circle the whole and the half-degrees are read, and the minutes are found by means of the vernier, which contains twenty-nine half-degrees divided into thirty parts.

The setting is made three times. If the temperature is constant the individual determinations should at most only differ among themselves by two to three minutes. Larger differences than this are almost always caused by temperature variation. The temperature of the liquid is, therefore, measured every time to $^1/_{10}°$ by the thermometer dipped in the liquid, and recorded in the table. Large variations are most simply avoided by allowing the liquid to remain in the room for some time, so that it can take the temperature of the room.

The density measurements which follow must be done at the same temperature as the refractive index measurement—most easily, therefore, at room temperature.

If it is desired to measure the refractive index at some temperature other than that of the room, then for setting the temperature the hollow jacketing vessel supplied with the instrument is used. This is fastened to the prism-holder by means of two metal pegs in such a way that it surrounds the

liquid container concentrically. Water from a thermostat set at the desired temperature is pumped through the jacketing tube by means of a circulating pump. The upper opening of the jacketing tube is closed by a cork, through a hole in which the thermometer dips into the liquid. When the degree of constancy of temperature required is less, water may be allowed to flow from a large vessel kept at the desired temperature, and standing above the jacketing tube.

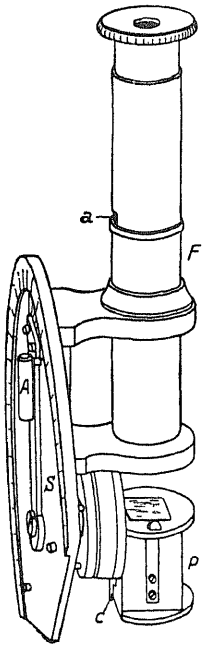

FIG. 40.

(β) *The Abbé Refractometer.* (1) *General.*—The Abbé refractometer has the advantage over the Pulfrich that only very small quantities of liquid are required for a measurement. Against this there is the disadvantage that it is not possible with this instrument to measure the temperature of the liquid accurately or to keep it constant. It is best, therefore, to work at room temperature, and to allow the liquid to stand in the room in which the measurement is to be made for at least half an hour before the measurement is made.

(2) The external construction is illustrated in Fig. 40, and the path of the rays in Fig. 41. One-half of the prism combination P can be removed by pressure upon the spring *c*. Solid bodies are laid with a smooth surface against the fixed prism. Liquids are put between the two prisms. Since with this instrument also the determination of the refractive index depends upon the measure-

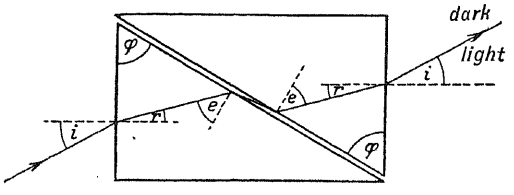

FIG. 41.

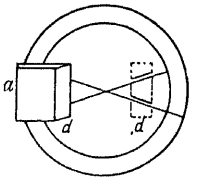

FIG. 42.

ment of the limiting angle for total reflection as the light passes from the prism into the substance to be measured, the refractive index of the latter must be smaller than that of the prism.

(3) *The Path of the Rays.*—The prism combination acts as a plane parallel plate (Fig. 41), i.e. the ray of light leaves the prism at the same angle with the normal as it enters. If now the prism is turned so that the angle at which the ray falls upon the boundary surface glass/liquid increases, the ray will continue to pass through the prism until the limiting angle of total reflection e at the boundary glass/liquid is reached. If the angle of incidence at this boundary surface exceeds the angle of total reflection the ray no longer passes from the glass into the liquid. The limiting angle of total reflection corresponds, therefore, to the line of separation light/dark in the field of view of the reading telescope. The cross-wires are set sharply on this line and the corresponding angle of emergence i read on the divided circle. With the vernier, minutes can be read. As a source of light a sodium-flame or other monochromatic light serves.

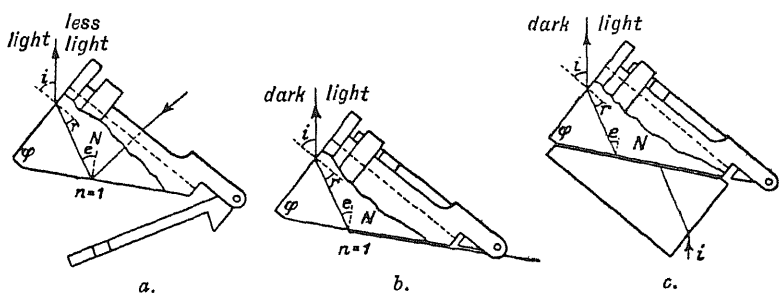

FIG. 43.

(4) *Determination of the Refracting angle φ of the Prism.*—This is done by setting the telescope perpendicular to each of the prism faces in turn. The manipulation is as follows: the telescope F, which is rigidly connected to the divided circle S, is held by the right hand between the two stays, while the movable arm A carrying the vernier, and on to the axis of which the double prism P is fastened, is turned. The reflected image of the cross-wires (illuminated through the auxiliary prism a) is brought into coincidence with the cross-wires (Fig. 42), for which purpose the small window a must be turned towards a brightly illuminated white wall, or to some extended source of light.

(5) *Determination of the Index of Refraction of the Prism.*—Figs. 43a, b, c show the path of the ray at total reflection in air, which is used to measure the refractive index of the prism. The angle to be determined (i) is that at which the limiting

ray for total reflection passes from the prism into the air. It can be seen from the sketch of the path of the rays that three different methods of illumination can be used for this purpose.

For the calculation of n (air/glass) e and r are eliminated from the fundamental equations:

$$n \sin e = 1\,; \quad e = \varphi - r, \; [\text{since } \varphi + (90 - r) + (90 - e) = 180^\circ]\,;$$

$$\sin i = n \sin r.$$

$$\sin i = n \sin (\varphi - e)\,;$$

$$\sin i = n (\sin \varphi \cos e - \cos \varphi \sin e) = n \sin \varphi \cos e - \cos \varphi\,;$$

$$\sin i + \cos \varphi = n \sin \varphi \sqrt{1 - \sin^2 e}$$

$$= n \sin \varphi \sqrt{1 - \frac{1}{n^2}}\,;$$

$$\frac{\sin i + \cos \varphi}{\sin \varphi} = \sqrt{n^2 - 1}.$$

The logarithmic calculation of n by this formula is simplified by writing instead of the left-hand side of the formula

$$\frac{\cos \varphi + \cos (90 - i)}{\sin \varphi} = \frac{2 \cos \dfrac{\varphi + (90 - i)}{2} \cos \dfrac{\varphi - (90 - i)}{2}}{\sin \varphi} \tan \psi,$$

$$n^2 - 1 = \tan^2 \psi$$

$$n^2 = \frac{\sin^2 \psi}{\cos^2 \psi} + 1 = \frac{\sin^2 \psi + \cos^2 \psi}{\cos^2 \psi} = \frac{1}{\cos^2 \psi}.$$

ψ is an auxiliary angle. The value of n is then found to be

$$n \text{ (air/glass)} = \frac{1}{\cos \psi} \quad . \quad . \quad . \quad (49)$$

(6) *Determination of the Refractive Index of a Liquid.*—A drop of the liquid is put on to the hypotenuse surface of the fixed prism, and the removable prism is then slid over it so that the liquid forms a thin layer between the two prisms. The angle i is now measured, at which the limiting ray for total reflection passes from the prism into the substance. The angle i is given the + or − sign according to whether the emergent ray is inclined away from or towards the refracting edge of the prism. From i, n and φ the refractive index n of the substance with respect to air is found by means of the equations:

$$n \text{ (liquid/glass)} = \frac{1}{\sin e}\,;$$

$$n\ (\text{air/liquid}) = \frac{n\ (\text{air/glass})}{n\ (\text{liquid/glass})} = n\ (\text{air/glass})\ .\ \sin e\ . \quad (50)$$

e is calculated from

$$e = \varphi - r$$

$$n\ (\text{air/glass}) = \frac{\sin i}{\sin r};\ \sin r = \frac{\sin i}{n\ (\text{air/glass})}.$$

(2) Measurement of Density with an Ostwald Pyknometer

(α) *Manipulation of the Pyknometer.*—The pyknometer is carefully dried by drawing air through it, and weighed on an analytical balance to $^1/_{10}$ mg. (Determine the zero of the balance and the sensitivity.) The pyknometer is then filled with water at room temperature, or at the temperature at which the measurement of refractive index was made. The point b (Fig. 44) is dipped into a beaker filled with distilled water, and the vessel is sucked full of water by means of a tube attached to the wide end of the pyknometer. In this preliminary filling it is unnecessary to pay attention to the etched mark a. The pyknometer is now hung for ten minutes in a beaker filled with water at room temperature or the temperature of the experiment; this beaker stands centrally in a wider beaker, so that between the two there is a layer of still air. When temperature equalisation is completed the temperature of the water is measured with a thermometer divided into tenths.

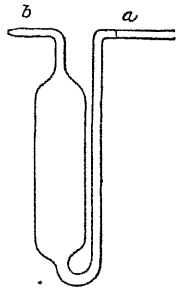

Fig. 44.

If now the pyknometer is full right up to the tapered end, but at the other, wider end the water is beyond the mark, the liquid meniscus is set on this mark by carefully touching the liquid at the tapered end with filter-paper. As soon as the exact setting is obtained, the tapered end is closed with a rubber cap (a short piece of rubber tubing with a short glass rod pushed into it), and then the other end similarly. (The movement of the liquid meniscus caused by this is due to the pressing in of the small quantity of air in the cap, and does not involve any alteration in the quantity of liquid contained.)

If, however, the pyknometer is not full up to the tapered end, but contains an air bubble there, the water-filled beaker together with the pyknometer is carefully tilted, so that water

begins to drop out of the tapered end; the tapered end is now again dipped into the water previously used for filling, and the apparatus slowly brought back into the horizontal position. In this way water is automatically drawn in from the storage vessel. A slight excess is allowed to enter, so that the mark is over-stepped, and the excess removed, as before, by touching with filter-paper. The pyknometer, closed with rubber caps, is then immediately taken out of the water, dried carefully outside with a soft, non-fluffy towel, and weighed to $^1/_{10}$ mg.

After removing the water the instrument is carefully dried inside and outside (inside, with absolute alcohol, ether, and by drawing air through) and filled with the liquid under investigation, following the same procedure and taking the same precautions as described for the filling with water. If the liquid is very volatile, the rubber caps can be put on even after the preliminary filling. The fine adjustment to the mark is done only after the filled pyknometer has been in water at the room temperature or the temperature of the experiment for ten minutes. It is then removed, dried outside, and weighed.

(β) *Calculation of the Density.*—The density denotes the weight of 1 c.c. of the liquid. The object of weighing the pyknometer with water is only to find the exact content by volume of the pyknometer at the temperature in question. The change in density of water must be taken into account; for this, reference should be made to the tables. It is simplest to use a table giving the volume of 1 gm. of water containing dissolved air, weighed in air with brass weights, in the range of temperature from 10° to 25° (see e.g., Ostwald-Luther, "Hand-und Hilfsbuch zur Ausführung physiko-chemischer Messungen," 4th ed., p. 186). Using the table, the volume of the pyknometer is found by multiplying the weight of water as found on the balance by the value in the table corresponding to the temperature. If, on the other hand, a table is used which gives the volume of 1 gm. of air-free water, weighed in a vacuum, the weight of water must first be corrected to vacuum; the table for this correction may be taken from Ostwald-Luther, 4th ed., page 80. The difference between air-free water and water containing air is so extremely small that it affects the density only in the sixth place, and may be neglected here.

The weight of the liquid under investigation must in any case be corrected to vacuum (cf. p. 3). The density required for this is calculated with sufficient accuracy by dividing the uncorrected weight of liquid by the uncorrected weight of water.

Scheme for the calculation:—

Weight of empty pyknometer :
Weight of pyknometer filled with water :
Weight of the water in air :
Volume of this quantity of water at the temperature of the experiment (from the tables) :
Weight of the pyknometer with the liquid under investigation :
Weight of the liquid in air :
Provisional density of the liquid :
Vacuum correction for the liquid :
Weight of the liquid in vacuum :
Density of the liquid at the temperature in question

$$= \frac{\text{Vacuum weight}}{\text{Volume of water}}.$$

(3) Calculation of the Molecular Refraction of an Organic Liquid or a Dissolved Salt

(α) After determining the refractive index, density, and specific refraction [(42), p. 125] of an organic liquid, the molecular weight and chemical composition of the liquid should be taken into account.

The molecular refraction is then calculated on the one hand from the specific refraction and the molecular weight, and on the other hand from the atomic refractions, using the values in the tables (e.g. Landolt-Börnstein). The values for the D line should be used, and attention paid to the kind of chemical bonds present.

(β) Two solutions of a salt, of known percentage compositions by weight, are prepared. (See that the salt is dry.) The refractive indices and densities are determined as described above. Let p be the concentration expressed as weight per cent. ; then from equation (46) the relationship holds :

$$\frac{n_s^2 - 1}{n_s^2 + 2} \cdot \frac{100}{d_s} = \frac{n_w^2 - 1}{n_w^2 + 2} \cdot \frac{100 - p}{d_w} + \frac{R_d \cdot p}{M}.$$

From this, R_d is determined, and compared with the sum of the corresponding ionic refractions (p. 127).

The refractive index of pure water should be determined at the same time. The density d_w will be found in the tables.

XIII. ABSORPTION OF LIGHT. QUANTITATIVE SPECTROPHOTOMETRY IN THE VISIBLE REGION

(a) Theory

(1) WHEN continuous light, that is light in which all wave-lengths of a definite spectral region are contained (white light in the wider sense) passes through a solid, liquid or gaseous substance, it is weakened—partly through reflection at the boundary surface of the substance, and partly by absorption in the interior of the substance. A body appears white, or grey, when all wave-lengths are reflected equally, and black when no light is reflected from the surface, and all wave-lengths are completely absorbed.

If all wave-lengths are equally weakened as the light is transmitted, the substance is colourless, or in the case of complete absorption, opaque. If only the light of a certain interval of wave-lengths is reflected or absorbed (partially or completely) the substance appears "coloured" by reflected or transmitted light. Our eyes are sensitive to the range of wave-lengths from 400 to 700 $\mu\mu$, and the properties "white, gray, black, colourless, opaque, coloured" are directly recognisable without any auxiliary means. For smaller wave-lengths, of 200 to 400 $\mu\mu$ (ultra-violet) a photographic plate or a photoelectric cell is required, and above 700 $\mu\mu$ (infra-red) a thermocouple is used.

(2) Quantitatively, the strength of absorption of monochromatic light by a homogeneous body—whether a single substance or a solution of definite concentration—depends upon the thickness of the layer, in such a way that through equal thicknesses of layer $d\mathrm{D}$ equal fractions $\frac{d\mathrm{I}}{\mathrm{I}}$ of the intensity of the light falling upon the layer in question are removed by absorption:

$$-\frac{d\mathrm{I}}{\mathrm{I}} = k'' \,.\, d\mathrm{D}. \quad \text{(Lambert's law.)}$$

For many solutions the constant k'' is proportional to the concentration of the dissolved substance:

$$-\frac{dI}{I} = k' \,.\, c \,.\, dD.$$

Integration of this equation (cf. pp. 102 and 104), when D denotes the finite thickness of the layer through which the radiation passes, I_0 the initial intensity and I the intensity of the light which gets through, gives

$$I = I_0 \,.\, e^{-k' \,.\, c \,.\, D} \quad . \quad . \quad . \quad . \quad (51)$$

In this case, then, the extent of the weakening depends (apart from k') only upon the magnitude of the product c . D, i.e. upon the amount of substance or the number of dissolved molecules, which are in the path of the light ray. (Beer's law.)

If the number 10 is taken as the base instead of e, then (51) becomes

$$I = I_0 \,.\, 10^{-kcD}, \quad . \quad . \quad . \quad (52)$$

in which $k = 0{\cdot}4343 \,.\, k'$, denotes the *decadic absorption coefficient.* D is measured in cm., and c in mol/lit. This constant k is a characteristic magnitude for the particular substance and the wave-length used. If a diagram is constructed with the different values of k as ordinates and the corresponding wave-lengths as abscissæ, then "absorption curves" are obtained (cf. Fig. 45), the form of which is specific for every transparent substance and the particular state in which it is. Changes in the state of a dissolved substance, e.g. dissociation, solvation, hydrolysis, can be inferred from changes in these curves. For example, if one studies methylorange first in strong acid solution (red colour) and then in alkaline solution (yellow colour), then corresponding to the difference in colour different absorption curves are found, which according to the simple Ostwald theory of indicators is explained by the fact that in the first case practically only the

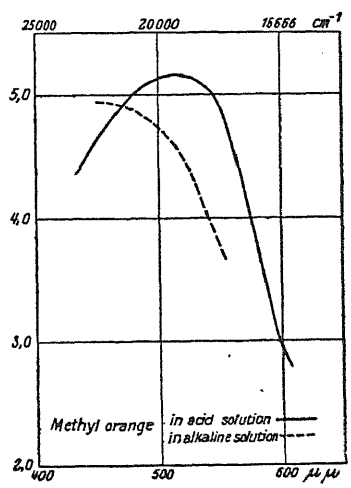

FIG. 45.

undissociated acid (red), and in the second practically only the dissociated salt (yellow anions) is present and causing absorption (cf. p. 66). If in a third experiment the p_H of the solution is arranged to be between 3 and 4 (cf. p. 67), then the indicator will be in its transition region and showing its transition colour (orange) since red and yellow forms are present in quantities of the same order of magnitude. Using the absorption curve determined for this third case the amounts in the yellow and red forms can be determined, i.e. the amounts in equilibrium with each other at the p_H chosen. If all three measurements are made in bulbs of the same thickness, then for every wave-length the absorption in the third case is additively determined by the absorption of the red and the yellow particles together. If c is the total concentration of the dye-stuff, c_r and c_y those of the red and yellow forms, respectively, and k_r, k_y and k_a the absorption constants determined in the first, second, and third experiments, for the wave-length considered, then

$$-\frac{dI}{dD} = (k_y' \cdot c_y + k_r' \cdot c_r)I;$$

$$I = I_0 \cdot 10^{-(k_y \cdot c_y + k_r \cdot c_r)D} = I_0 \cdot 10^{-k_a \cdot c \cdot D},$$

where $$k_a \cdot c = k_y \cdot c_y + k_r \cdot c_r.$$

Substituting $$c_r = c - c_y$$

$$k_r \cdot c - k_r \cdot c_y + k_y \cdot c_y = k_a \cdot c;$$

$$c_y = \frac{c(k_a - k_r)}{k_y - k_r} \quad . \quad . \quad . \quad . \quad (53)$$

(3) The absorption coefficient is measured as follows: a monochromatic light beam is divided into two parallel beams, of which one passes through an absorption tube containing pure solvent and the other through an absorption tube of equal thickness containing the solution of known concentration. The weakening suffered by the second beam by absorption in the solution is measured by decreasing the intensity of the other beam by means of a rotating sector of variable aperture to the same extent, so that the two light beams appear equally bright. (The sector must rotate at least thirty times a second, otherwise the intermittent weakening does not appear to the eye to be a uniform weakening.) The extent of the weakening is given by the ratio of the angle of the sector to 360°. With a sector opening of 36° the light intensity is reduced to one-tenth of the original value. In moving across the spectrum the absorptive power usually changes *continuously*, so that instead

of measuring the weakening for some definite wave-length and concentration by the alteration of the sector opening, conversely the wave-length and concentration may be found, for which the light is weakened in the ratio determined by a setting of the opening of the sector. If a spectroscope with a narrow eye-piece slit (monochromator) is used to obtain the monochromatic light, then the various spectral regions can be selected from white light simply by moving the prism or the eye-piece tube; in this way the particular region can be found in which the two light beams weakened one by the rotating sector and the other by the solution appear equally bright. Ultimately it is necessary to alter the concentration of the solution.

(4) The calculation of k is made as follows: If λ is the wave-length for which the light is weakened exactly to one-tenth by the solution of concentration c and thickness of layer D (the proportionate decrease in intensity being governed by the setting of the sector opening), then

$$I = I_0 \,.\, 10^{-1} \text{ (solvent and sector)}$$
$$I = I_0 \,.\, 10^{-k \cdot c \cdot D} \text{ (solution)};$$
$$1 = k \,.\, c \,.\, D; \quad k = \frac{1}{c \,.\, D} \quad . \quad . \quad . \quad . \quad (54)$$

According to the choice of c and D various values can be determined for k. When the absorption is a maximum k is largest, and the product $c \,.\, D$ smallest. If this product is made smaller (by decrease in c or D) than corresponds to the maximum, then there is no longer any position in the spectrum where equality of brightness of the two beams can be found; the solution cell remains brighter in all regions of the spectrum than the comparison field which has been weakened to $^1/_{10}$th.

References :—
Eucken, Jette, and Lamer. § 355.
Nernst. Bk. II, Chap. VI, p. 396 *seq.*

(b) Experimental

(1) *Apparatus.*—Fig. 46 shows the arrangement of the different parts of the apparatus: L is a glow-lamp with the filament wound into the form of a pencil, which serves as a source of white light. K is a condensing lens of about 15 cm. focal length, which throws an image magnified about 1·5 times upon the objective slit of the spectroscope SS. A matt glass plate Ma is introduced immediately behind K. At a distance of a few cm. from the condenser stands a small table carrying

the two cells with the pure solvent (LM) and with the solution (LK). By means of the two Fresnel prisms FP the two light beams passing through the cells are brought into juxtaposition. The lens L*i* draws out the line of separation of the Fresnel prisms to a visible width. All parts of the apparatus mentioned so far are mounted on an optical bench. SS is the objective slit of the spectroscope, KL the collimating lens, P the prism, OL the objective lens, and OS the eye-piece slit. A sector S (cut out of glazed cardboard) is introduced between the sheet of matt glass and the cell LM containing the solvent; the sector is mounted on the axle of an electric motor (of more than 1000 revs. per min.).

Since the slit SS is in the focal plane of the collimating lens KL, and the eye-piece slit in that of the objective lens OL, the

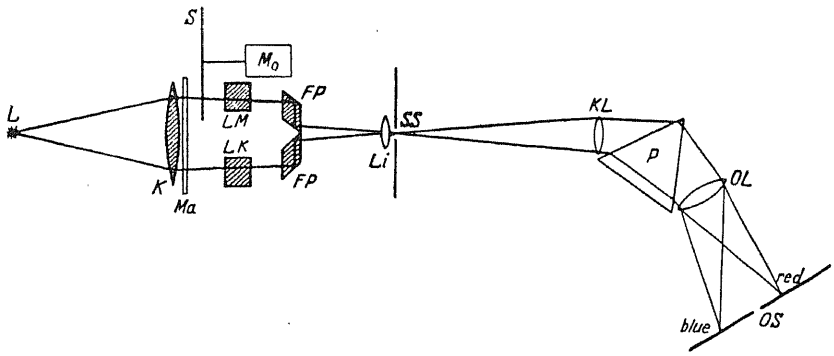

FIG. 46.—Spectrophotometer.

eye when applied directly to the eye-piece slit, sees objects lying in front of the slit SS in their natural size and shape, but in the colour corresponding to the position in the spectrum of the eye-piece slit. Thus if the cells are properly arranged, the two comparison fields brought together by the Fresnel prisms are seen in the spectral colour desired and with a brightness corresponding to the transparency of the solvent or of the solution. If now a sector which allows 10 per cent. of the light to pass is rotated in front of the solvent and the eye-piece slit is moved across the spectrum, then at some definite wave-length there will be an interchange of light and dark in the fields which are being compared. This wave-length is the position in the spectrum where the two fields are equally bright. By moving the eye-piece slit to and fro several times it can be determined very exactly. It may happen that there are several

places in the spectrum of equal brightness; if on the other hand none can be found, then either c or D or the sector aperture must be altered.

(2) *Experimental Procedure.* (α) *Calibration of the Spectroscope.*—The telescope which carries the eye-piece slit of the spectroscope can be turned by means of a micrometer screw. According to the position of the micrometer screw light of different wave-lengths leaves the eye-piece slit. The wave-length corresponding to a definite setting is determined as follows: light of precisely known wave-lengths in different parts of the spectrum is produced, and the telescope is set by means of the micrometer screw that a particular spectral line lies exactly in the middle of the eye-piece slit (which is about 1 mm. wide), and the corresponding position of the micrometer screw is read. By plotting these positions on millimeter paper as ordinates against the corresponding wave-lengths as abscissæ, a smooth curve is obtained, the "dispersion curve" of the spectroscope.

Light of different precisely known wave-lengths is produced by means of vacuum tubes containing hydrogen, helium, or mercury, through which the discharge of a small spark coil is sent. The wave-lengths are obtained from the tables (e.g. Landolt-Börnstein).

(β) *Measurement of the Absorption of Light by Solutions.*—The optical bench carrying the light source, the condenser, and the empty cells is set in the optical axis of the collimator tube; then looking through the eye-piece slit, the spectroscope is moved until the line of separation of the two Fresnel prisms bisects the field of view and the two halves appear equally bright. The stand with the motor and sector is then brought up at the side so that the cell containing the solvent is just covered by the sector, without the latter touching anywhere. All the work is done with a sector opening of 36°, so that the light is diminished to one-tenth of its original intensity. The relationship deduced above (54) then holds: $k = \frac{1}{c \cdot D}$.

500 c.c. of each of the following solutions is prepared: $\frac{M}{10000}$ methyl-orange in $\frac{N}{2}$ HCl; $\frac{M}{10000}$ fuchsine or malachite-green in distilled water, and an $\frac{M}{10}$ permanganate olution. The wave-lengths of equal brightness are then looked for, in 2, 5, 10 and 20 mm. cells. The solutions are then diluted with

water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{10}$; if the substance remains chemically unaltered on dilution, the measurements of the diluted solutions in the appropriate cells must all give the same brightness as the original solution in the 2 mm. cell

$$\left(\text{Beer's law: } k \,.\, c \,.\, \mathrm{D} = k \,.\, \frac{c}{2} \,.\, 2\mathrm{D} = k \,.\, \frac{c}{4} \,.\, 4\mathrm{D} = k \,.\, \frac{c}{10} \,.\, 10\mathrm{D}\right).$$

The series of diluted solutions are also measured in the cell with the smallest thickness, until the cell containing the solution remains brighter in all parts of the spectrum than the comparison field (weakened to $^1/_{10}$). If necessary, a further tenfold dilution of the solution must be made. Finally the logarithms of k are plotted as ordinates against the corresponding wave-lengths as abscissæ, so obtaining the "logarithmic absorption curve."

The absorption spectrum of methyl-orange should also be measured in alkaline solution $\left(\frac{\mathrm{N}}{2}\mathrm{KOH}\right)$ as an example of the optical change in a substance resulting from chemical change. In a third experiment $\frac{\mathrm{N}}{5000}$ HCl is used as a solvent. Using the absorption curves, the concentration of undissociated and dissociated molecules can be calculated by (53), and also the dissociation constant of methyl-orange (p. 155).

XIV. ULTRA-VIOLET SPECTROGRAPHY

(a) Emission spectra of metals in the ultra-violet

THE optical bench is assembled with a small quartz spectrograph, a quartz condensing lens and the stand for the spark electrodes. With a spark coil and Leyden jar in parallel a spark is produced between zinc rods, and the stand is adjusted so that an image of the spark is thrown by the condensing lens on to the slit of the spectrograph. The image should not be sharp, but should be about the size of the slit, as can be arranged by moving the carriage of the condensing lens. Consecutive exposures are then taken of 5, 10, 30 and 60 seconds' duration. The plate is developed with, say, commercial metol-hydroquinone developer, and from this negative there will be no difficulty in selecting the correct time of exposure. Using this, the spectra are taken of sparks between rods of Cu, Cd, Al, Ni, Fe; in addition, using the diaphragm with two holes, Cu and Al are taken side by side, and Cu and Ni. In Al and Ni the strongest Cu lines can be seen quite clearly, in spite of the very large number of lines present (especially with Ni). For small amounts of admixed metals, this analysis can be so improved as to be almost quantitative. By means of a standard plate which has the wave-lengths marked on it (an iron arc spectrum is very suitable because of its richness in lines) the position of the different lines and the extension of the spectra into the ultra-violet and visible regions can be ascertained. Orthochromatic plates can also be used, and compared with ordinary plates.

(b) Qualitative investigation of the absorption of some substances in the ultra-violet

Iron electrodes are put into the electrode stand, and with the apparatus used in the previous experiment exposures are taken with a quartz plate, a glass plate, and a Uviol glass plate

in front of the slit; also with the quartz cell containing in one case distilled water, then an $\frac{M}{20}$ K_2CrO_4 solution and finally an $\frac{M}{2}$ solution of benzene in alcohol, the number of each exposure being recorded. With the aid of the standard plate the line 310 $\mu\mu$ is found in the iron spectra, and relative to this the limits of absorption by the different substances is stated. With the benzene solution exposures are also made in a "Baly tube," using thicknesses of 2, 5, 10, 20 and 50 mm.; the "absorption limit curve" is then drawn, by plotting the logarithms of the thickness as ordinates against the wave-lengths as abscissæ.

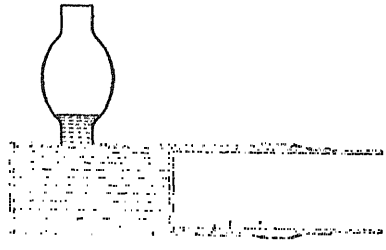

FIG. 47.—"Baly tube."

Care should be taken when pushing inwards the moving part of the Baly tube, not to knock the quartz window out. After use it should be cleaned at once.

References :—

Eucken, Jette, and Lamer. §§ 304; 308; 327-35.

ELECTRICAL MEASUREMENTS

General

(1) THE MOST IMPORTANT PRACTICAL ELECTRICAL UNITS

Quantity of electricity: The unit is 1 coulomb = 1 ampère × 1 second.

1 coulomb is the quantity of electricity which precipitates 0·001118 gm. silver from a solution of $AgNO_3$.

1 coulomb = $3 \cdot 10^9$ electrostatic units = 0·1 electromagnetic units.

1 elementary unit of electricity = charge of 1 electron
= $1 \cdot 59 \cdot 10^{-19}$ coulomb
= $4 \cdot 77 \cdot 10^{-10}$ electrostatic units.

1 electrochemical equivalent = 1 faraday

$$= \frac{107{\cdot}88 \text{ (A. wt. of silver)}}{0{\cdot}001118} = 96{,}494 \text{ coulombs} = 1\text{F}.$$

Current strength: The unit is 1 ampère $= \frac{1 \text{ coulomb}}{1 \text{ second}}$.

1 ampère is the strength of current such that in 1 second 1 coulomb flows through the cross-section of the conductor.

Electrical resistance: The unit is 1 ohm.

1 ohm is the resistance of a mercury column of 106·300 cm. length and 1 sq. mm. cross-section at 0° C. (The mass of this column = 14·4521 gm.)

1 ohm $= \frac{1}{9} \cdot 10^{-11}$ electrostatic units
$= 10^9$ electromagnetic units.

Electrical potential, electromotive force, potential difference: the unit is 1 volt.

1 volt is the potential difference existing at the ends of a conductor of 1 ohm resistance when a current of 1 ampère is flowing in it.

1 volt $= \frac{1}{300}$ electrostatic units $= 10^8$ electromagnetic units.

Electrical work: The unit is 1 volt × 1 coulomb = 1 joule = 1 watt-second.

1 joule is performed when 1 coulomb flows through a fall of potential of 1 volt.

1 joule $= 10^7$ ergs.

1 kilowatt-hour = 3,600,000 joules.

Electrical power: The unit is 1 volt × 1 ampère = 1 watt.

1 watt is the power produced by a current of strength 1 ampère when flowing through a fall in potential of 1 volt.

1 watt $= \frac{1 \text{ joule}}{1 \text{ second}}$.

1 H.P. = 735·5 watts.

Electrical capacity: The unit is 1 farad $= \frac{1 \text{ coulomb}}{1 \text{ volt.}}$.

A condenser has a capacity of 1 farad when it is charged to a potential of 1 volt by 1 coulomb.

1 farad $= 10^6$ microfarads $= 9 \cdot 10^{11}$ electrostatic units
$= 10^{-9}$ electromagnetic units

Further details about the connexions between these practical units and those of the electrostatic and electromagnetic systems will be found in any standard text-book of Physics.

(2) Ohm's Law

$$J = \frac{E}{W} \quad . \quad . \quad . \quad . \quad (55)$$

Current strength (usually in ampères)

$$= \frac{\text{Potential difference (usually in volts)}}{\text{Resistance (usually in ohms)}}.$$

This law applies to the whole current circuit and to every individual part of it. If, for example, there is a potential difference of 2 volts over a total resistance of 50 ohms, then the current strength is $\frac{2}{50} = 0{\cdot}04$ ampère. Over a part of the resistance of 10 ohms there is, of the total fall in potential, only the part $E' = 0{\cdot}04$ ampère $\times$ 10 ohms $= 0{\cdot}4$ volt. In this connexion, reference should be made to the Wheatstone bridge circuit (p. 157), to the Poggendorf compensation method (p. 183) and to what is said on page 226 concerning the E.M.F. on closed circuit.

(3) Poles

Usually the poles on accumulators or switch terminals are marked + and —. Failing this, or if there is some doubt as to the correctness of the marks, they can be determined by the aid of "pole testing paper." For this purpose filter paper soaked either in starch-iodide solution or in a solution of phenolphthalein or blue litmus and any electrolyte, e.g. sodium sulphate or chloride, is used. At the positive pole there is either oxidation of the iodide ion and a brown coloration through precipitated iodine (or blue through the starch iodide) or discharge of OH' and reddening of the litmus through the excess of $H^{\cdot}$. At the negative pole $H^{\cdot}$ is discharged and the phenolphthalein reddens through the excess of OH'. The test is carried out by placing the moist pole testing paper upon a clean sheet of glass, and bringing the ends of the leads for a few seconds on to the test paper. With voltages of 110 or more the distance separating the ends should be at least 1 cm., and with smaller voltages, a smaller distance. The colour is easily recognisable on removing the wires.

Kathode and anode; + and — poles. In a cell through which current is flowing, the cathode is by definition the electrode to which the cations wander; the anode is the electrode to which the anions wander; it is immaterial whether the cell is functioning as a galvanic element or as an electrolytic cell.

The *sign* of the cathode or anode depends, however, upon whether the cell is a galvanic element or an electrolytic cell.

In a current-producing galvanic element the sign of the electrodes and the direction of migration of the ions are determined by the chemical or osmotic process going on. In this case that electrode is positive to which the cations in the solution migrate and at which they discharge—the cathode, therefore. The anode is correspondingly charged negatively. In the galvanic element the cathode is the $+^{ve}$ pole, the anode the $-^{ve}$ pole.

But with an electrolytic cell an *external* electromotive force causes the charging of the electrodes and therefore the migration of the ions. The electrode which is connected to the positive pole of the external source of current becomes positively charged, and the anions migrate to this in the solution; here the positive pole is the anode, and similarly, the negative pole is here the cathode.

(4) Connexions

(α) If accumulators are connected "in series" (+ pole of the first to the — pole of the second, + pole of the second with the — pole of the third and so on), then the resultant total E.M.F. = the sum of all the individual E.M.F.'s:

$$E = E_1 + E_2 + E_3 \quad . \quad . \quad . \quad (56)$$

When accumulators of the same E.M.F. are connected "in parallel" (by connecting together all the + poles on the one hand, and all the — poles on the other) the total E.M.F. remains unaltered and equal to that of one accumulator; but in this case a maximum current strength may be taken from the battery equal to the sum of the current strengths which may be taken from the individual accumulators (in accordance with instructions for their use).

(β) If several resistances are connected *in series* in a circuit, the total resistance is equal to the sum of the separate resistances:

$$W = W_1 + W_2 + W_3 \quad . \quad . \quad . \quad (57)$$

If the resistances are connected in parallel, the total *conductivity* of the group is equal to the sum of the conductivities of the separate resistances. Conductivity is the reciprocal of resistance and is measured in reciprocal ohms Ω^{-1}. Thus with the connexion in parallel

$$\frac{1}{W} = \frac{1}{w_1} + \frac{1}{w_2} + \frac{1}{w_3} \quad . \quad . \quad . \quad . \quad (58)$$

$$W = \frac{w_1 \cdot w_2 \cdot w_3}{w_1 \cdot w_2 + w_1 \cdot w_3 + w_2 \cdot w_3}.$$

The corresponding expression for two resistances is

$$W = \frac{w_1 \cdot w_2}{w_1 + w_2} \quad . \quad . \quad . \quad (59)$$

With a series connexion the same strength of current flows in every resistance. With a parallel connexion the current strengths in the separate current paths are proportional to the conductivities or inversely proportional to the resistances:

$$i_1 : i_2 = \frac{1}{w_1} : \frac{1}{w_2} = w_2 : w_1 \quad . \quad . \quad . \quad (60)$$

(γ) Ammeters are connected directly in the current circuit; since their internal resistance is always very small, their introduction hardly affects the current strength.

Voltmeters are connected in parallel with the conductor across which it is desired to determine the potential difference; they are in a "shunt" circuit. Unlike ammeters, they are made with a very large internal resistance (1000 ohms or more). If the resistance of the conductor is small compared with that of the voltmeter, the introduction of the latter alters the potential to be measured only very slightly.

Because its own resistance is very small, an ammeter must only be connected to a source of current when a sufficiently large resistance is included at the same time; a voltmeter can be connected directly to a source of current provided that the potential difference of the latter lies within the range of the instrument.

References :—
Eucken, Jette, and Lamer. §§ 266-68.
Nernst. Bk. II, Chap. X.
Le Blanc. Chap. I.

XV. ELECTRICAL CONDUCTIVITY OF ELECTROLYTES

A. DETERMINATION OF THE AFFINITY CONSTANT OF AN ORGANIC ACID

(a) Theory

(1) WHILST in conductors of the first class (metals) the flow of the electric current consists in the movement of *electrons* in the direction of the negative current, in conductors of the second class (electrolytes) the transport of current consists in the movement of electrically charged material particles of both signs (the ions). The positively charged cations migrate in the direction of the positive current, and the negatively charged anions in the direction of the negative current. The current strength (= quantity of electricity per second) is governed by the total number of electric charges which move through a cross-section of the electrolyte in unit time. This depends upon the *migration velocity*, the *valency*, and the *concentration* of the kinds of ions involved, as is shown in the following more detailed consideration. Suppose that a potential difference of 1 volt is applied to the electrodes, which are separated by 1 cm.; then there exists in the interior of the electrolyte a uniform electric field of strength 1 volt per cm. The force upon the charged ions in this field causes, for the first moment, an accelerated movement of the ions, which, however, quickly becomes a uniform motion with constant velocity as soon as the frictional resistance experienced by the ions in their passage through the solvent, which increases with the velocity of movement, becomes as great as the driving force. Since the inner friction of the solvent decreases with increasing temperature, a rise in temperature diminishes the frictional resistance; equality between the frictional resistance and the driving force is then only reached at a somewhat greater ionic velocity; hence the ionic velocity and with it the conductivity (for a constant number of ions) increases with increase in temperature: in aqueous solutions at ordinary temperatures, usually by about 2 per cent.

per 1° C. Temperature affects the degree of dissociation as well as the mobility of the ions. According to the sign of the heat of dissociation an increase or a decrease of the dissociation may take place, with increase of temperature. In the latter case, if the influence of the decreasing dissociation outweighs that of the increasing mobility, the conductivity will decrease with rise in temperature.

(2) At a definite temperature, in an electrolyte containing two kinds of ions, let u cm./sec. be the absolute rate of migration of the positive ions in the electric field of 1 volt/1 cm., so that in a field of E volts/cm. it is $E \cdot u$ cm./sec. Suppose that there are n^+ positive ions in a 1 c.c. cube, imagined to be inside a larger volume of the electrolyte. Then in 1 second $n^+ \cdot E \cdot u$ ions pass through a cross-section of 1 sq. cm. perpendicular to the direction of the current, since ions distant from the cross-section in question by $E \cdot u$ cm. at the beginning of the second will have just passed through by the end of the second. A univalent ion carries the charge $\frac{F}{N}$ coulombs (F=Faradays equivalent = 96,494 coulombs; N = Avogadro's number = $6{\cdot}06 \times 10^{23}$), a ν^+ — valent ion carries $\nu^+ \cdot \frac{F}{N}$ coulombs. There will be, therefore, in one second, transported through the cross-section $\nu^+ \cdot \frac{F}{N} \cdot n^+ \cdot E \cdot u$ coulombs. If ν^-, n^-, and v be the corresponding values for the negative ions, then they will transport in the same time in the opposite direction $\nu^- \cdot \frac{F}{N} \cdot n^- \cdot E \cdot v$ coulombs. Since the movement of positive electricity in one direction is equivalent to the movement of negative electricity in the opposite direction, the total amount of current is obtained by adding the separate amounts of electricity carried by the two kinds of ions. The total transport in coulombs per second, or the current strength J in ampères is therefore

$$J = F \cdot E \left(\frac{n^+}{N} \cdot \nu^+ \cdot u + \frac{n^-}{N} \cdot \nu^- \cdot v \right) . \qquad (61)$$

If other kinds of ions are present, then for each there is a corresponding term inside the bracket.

The letter c_i will be used for $\frac{n}{N}$, the number of ions in 1 c.c. divided by the number of ions in 1 mol, i.e. the ionic concentration in mols per c.c.

Taking E over to the left-hand side of the equation, an expression is obtained for $\frac{\text{J (ampères)}}{\text{E (volts)}}$, which according to Ohm's law $= \frac{1}{W}$ = the conductivity in reciprocal ohms (Ω^{-1}).

$$\frac{J}{E}=\frac{1}{W}=F(c_i^+ . \nu^+ . u+c_i^- . \nu^- . v)=\text{specific conductivity}=\chi. \quad (62)$$

The conductivity calculated in this way of a 1 c.c. cube of electrolyte, measured between electrodes of cross-section 1 sq. cm. and separated by 1 cm., is called the "specific conductance," and is usually denoted by χ.

If a potential difference E is applied to electrodes of cross-section q sq. cm. and separated by d cm. in any vessel, then the ionic velocity in the field $\frac{\text{E volts}}{d \text{ cm.}}$ is u (or v) $. \frac{E}{d}$; q times as many ions move through the cross-section of q sq. cm. as through 1 sq. cm.; hence

$$J = q . \frac{E}{d} . F(c_i^+ . \nu^+ . u + c_i^- . \nu^- . v)$$

or

$$\frac{J}{E} = \frac{1}{W} = \frac{q}{d} . F . (c_i^+ . \nu^+ . u + c_i^- . \nu^- . v) = \frac{q}{d} . \chi = \frac{1}{C} . \chi. \quad (63)$$

The conductance of an electrolyte between electrodes of q sq. cm. cross-section and separated by d cm. is thus $\frac{q}{d}$ times as great as its specific ($q = 1$ sq. cm.; $d = 1$ cm.) conductance. Conversely, its resistance is $\frac{d}{q}$ times greater than its specific resistance σ, just as with conductors of the first class, for which also $W = \sigma . \frac{d}{q}$. The magnitude $C = \frac{d}{q}$ is called the "resistance capacity" or "cell constant" since it defines how many times greater the resistance in any given vessel is than when measured in a unit vessel.

In practice C is not determined by measuring up d and q, but empirically in the conductivity cell in question, by measuring the resistance of a solution for which specific conductance is accurately known. Then from (63) $C = \chi . W$. Then by means of C the specific conductance of all other electrolytes can be calculated from the conductivity measured in the conductivity cell in question: $\chi = \frac{C}{W}$.

For binary, uni-univalent electrolytes, e.g. KCl, $c_i^+ = c_i^-$ and $\nu^+ = \nu^- = 1$. The specific conductance then becomes (putting $c_i^+ = c_i^- = c_i$)

$$\chi = c_i F(u + v) \quad . \quad . \quad . \quad (64)$$

Introducing instead of the ionic concentration c_i the concentration of dissolved electrolyte c_e, also expressed in mol/c.c., then the relationship between the two quantities, for weak electrolytes, is given by the degree of dissociation: $c_i = c_e \cdot \gamma$.

Hence for the specific conductance

$$\chi = c_e \cdot \gamma \cdot F(u + v) \quad . \quad . \quad . \quad (65)$$

(3) The "molar conductance Λ_v" is defined as the conductivity of 1 mol of dissolved electrolyte, measured between electrodes 1 cm. apart and of cross-section such that for the given concentration the volume of solution containing the 1 mol is included between them. Hence the molar conductance is obtained from the specific conductance by multiplication by the volume expressed in c.c. in which 1 mol of the electrolyte is dissolved at the dilution or concentration in question:

$$V = \frac{1}{c_e};$$

$$\Lambda_v = \chi \cdot V \text{ (mol volume in c.c.)} = F \cdot \gamma \cdot (u + v) \quad . \quad (66)$$

At infinite dilution the electrolyte is completely dissociated, γ therefore $= 1$. The molar conductance is then

$$\Lambda_\infty = F \cdot 1 \cdot (u + v) \quad . \quad . \quad . \quad (67)$$

This is the highest value which the molar conductance can reach, and the value to which it tends with increasing dilution (V). It can often be determined with sufficient accuracy by extrapolation.

From the relationship

$$\frac{\Lambda_v}{\Lambda_\infty} = \frac{F \cdot \gamma \cdot (u + v)}{F \cdot 1 \cdot (u + v)} = \gamma \quad . \quad . \quad . \quad (68)$$

it follows that with weak electrolytes the degree of dissociation γ can be found from the ratio of the molar conductance when 1 mol is dissolved in V c.c. to the molar conductance at infinite dilution.

With *strong electrolytes* the value of $\frac{\Lambda_v}{\Lambda_\infty} = f_\lambda$ (called the conductance ratio) falls below 1 at finite concentrations (increasingly

as the concentration increases) even though the dissociation is practically complete, because of the electrostatic attraction between the ions (see p. 16).

(4) The single quantities from which Λ_∞ is made up additively according to the formula

$$\Lambda_\infty = \mathrm{F} \,.\, u + \mathrm{F} \,.\, v = \Lambda_{\text{cation}} + \Lambda_{\text{anion}} \quad . \quad . \quad (69)$$

are called by Kohlrausch the "*equivalent conductances*" of the kinds of ions in question. How large the separate quantity appropriate to each kind of ion is, cannot be ascertained by conductivity measurements alone; these give only the sum of the two quantities. But by means of the transport number (see p. 168) the ratios $\frac{u}{u+v}$ and $\frac{v}{u+v}$ can be determined, so that by a combination of both methods the separate ionic conductances can be found. At $t = 18°$ C. values for Λ are:

$$K^{\cdot} = 64{\cdot}2\,;\ Na^{\cdot} = 43{\cdot}0\,;\ Ag^{\cdot} = 54{\cdot}3\,;\ H^{\cdot} = 315\,;\ Cl' = 65{\cdot}3\,;$$
$$NO_3' = 61{\cdot}7\,;\ OH' = 174. \quad \Omega^{-1}\ \text{cm.}^2$$

It is immediately obvious from equation (69) that by dividing the mobilities of the separate ions by F, the actual migration velocities u or v in a field of 1 volt/cm. are obtained.

$$u\ (\text{cm. sec.}^{-1}\ \text{volt}^{-1}) = \frac{\text{equivalent conductance}\ (\Lambda_{\text{cation}})}{96494\ \text{coulombs}} \qquad (70)$$

With organic acids having large molecules Λ_∞ is related in a simple way to the number of atoms in the molecule. Values of Λ_∞ are:

For acids with		12	atoms at	25°	.	.	.	376	Ω^{-1} cm.^{2}
,,	,,	15	,,	,,	.	.	.	373	,,
,,	,,	18	,,	,,	.	.	.	371	,,
,,	,,	22	,,	,,	.	.	.	369	,,
,,	,,	25	,,	,,	.	.	.	368	,,
,,	,,	30	,,	,,	.	.	.	367	,,

These values are obtained, not by using the pure acids, which even at very great dilution are only partially dissociated, but from the strongly dissociating Na or K salts, subtracting the mobility of $Na^{\cdot}$ or $K^{\cdot}$ from Λ_∞ for the alkali salt (obtained by extrapolation). To the quantity obtained in this way as the conductance of the acid anion the value of the equivalent of $H^{\cdot}$ is added.

(5) *Ostwald's Dilution Law.*—On the basis of the relationship (68) $\frac{\Lambda_v}{\Lambda_\infty} = \gamma$ a simple method presents itself for determining

the degree of dissociation at different dilutions, by means of conductivity measurements. In this way the validity of the law of mass action for the equilibrium between ions and undissociated molecules can be tested—at least for weak electrolytes (e.g. weak acids or bases) where the absolute concentration of ions is sufficiently small to make the influence of the electrostatic forces acting between them practically negligible.

Let the concentration of a uni-univalent electrolyte be 1 mol in V litres, and the degree of dissociation γ; then the concentration of ions $C_i = \frac{\gamma}{V}$, and of undissociated molecules $C_u = \frac{1-\gamma}{V}$, mol/litre. According to the law of mass action

$$\frac{\frac{\gamma}{V} \times \frac{\gamma}{V}}{\frac{1-\gamma}{V}} = K \quad \text{or} \quad \frac{\gamma^2}{(1-\gamma)V} = K \quad . \quad . \quad (71)$$

This special form of the law of mass action for the case of an ionic equilibrium is known as "Ostwald's dilution law." K is called the "electrolytic dissociation constant" of the electrolyte. With acids it is a measure of the strength, and for all concentrations it makes possible a calculation of γ and hence of the concentration of the ions, in particular of the hydrion. In the case of acids K is usually referred to as the "affinity constant."

For rough calculations the simplified form of Ostwald's dilution law is often very useful, which can always be applied without serious error when γ is very small. In this case $1 - \gamma$ in the denominator can be replaced by 1, leading to the simple relationship:

$$\gamma^2 = K \,.\, V; \; \gamma = \sqrt{K \,.\, V} \quad . \quad . \quad (72)$$

In the literature the value of 100 K is usually given. The volume V is expressed in litres (unlike (66)).

In the following experiments the molar conductance Λ_v of an acid at different concentrations is determined; from the results and from the value of Λ_∞ the various values of γ are calculated, and finally by substituting corresponding values of γ and V in the Ostwald dilution law, the affinity constant of the acid is found.

References :—
Eucken, Jette, and Lamer. §§ 182-92; 242-50.
Nernst. Bk. II, Chap. VIII, pp. 415-24. Bk. III, Chap. I; Chap. IV. Bk. IV, Chap. VI.
Le Blanc. Chap. III, Chap. V, pp. 85-105.
H. S. Taylor. Chap. XI.

(b) Experimental

(1) Method of Measurement

Since conductivity $= \frac{1}{\text{Resistance}}$, the problem is the measurement of resistances. The value of an unknown resistance is found by comparing it with known resistances in a Wheatstone bridge circuit. The principle of the arrangement is shown in Fig. 48. A is a source of current, G a null instrument which indicates the absence of any current flowing in the conductor *ab*. This will be the case when there is no potential difference between *a* and *b*. The conditions for this are as follows: the potential fall E across the terminals of the source A takes place in two ways: along *cad* and along *cbd*. (The connecting wires from A to *c* and to *d* are so thick that their resistance and therefore also the fall of potential along them, is negligible.)

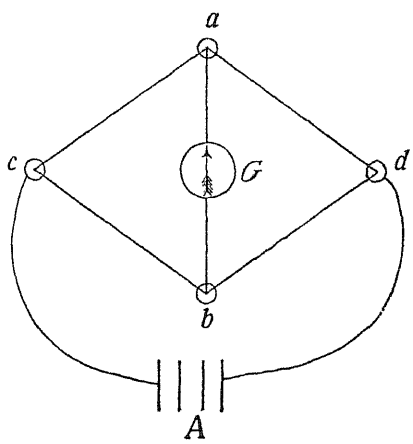

Fig. 48.

According to Ohm's law, which holds for both of the complete circuits $[E = i_1 (ca + ad) = i_2 (cb + bd)]$ and for their separate parts: the fall of potential along the resistance *ca* is $E \cdot \frac{ca}{ca + ad}$; and along *cb* is $E \cdot \frac{cb}{cb + bd}$. These two quantities will be equal, and accordingly there will be no potential difference between *a* and *b*, if

$$\frac{ca}{ca + ad} = \frac{cb}{cb + bd}, \text{ or } \frac{ca + ad}{ca} = \frac{cb + bd}{cb} \text{ or } 1 + \frac{ad}{ca} = 1 + \frac{bd}{cb}$$

or $ad : ac = bd : bc$. If *bc* is the unknown resistance and *ad*, *ac*, and *bd* are known, then when no current flows through G

$$bc = \frac{ac \cdot bd}{ad} \quad . \quad . \quad . \quad . \quad (73)$$

In order to avoid electrolysis and the consequent polarisation, alternating current is used, with a telephone as the null

instrument. The arrangement is shown in Fig. 49. *ab* is a measuring wire of manganin or platinoid, which is tightly stretched over a mm. measuring rule 1 m. long; the sliding contact *d* moves along this. R is a resistance box, W the conductivity cell containing the liquid to be measured. A is an accumulator which provides the current for the primary winding of the induction coil I. The secondary current is led on one side to the sliding contact *d*, and on the other side to the branching connection *c*, for which one of the terminals of the resistance box is conveniently selected. T is a telephone. In R any resistance is unplugged, and the sliding contact is moved until the sound in the telephone is a minimum. Com-

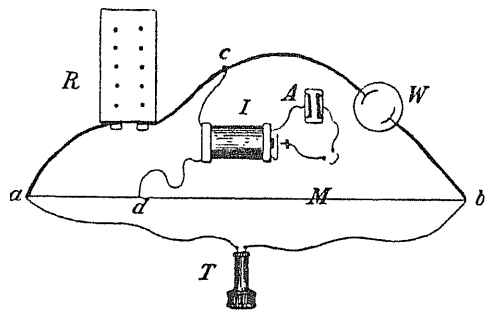

FIG. 49.

plete silence is not obtained, since this would require not only the proper ratio of the resistance, but also of the capacity and self-induction in the separate branches. From the setting of the bridge which gives the minimum, according to (73)

$$W = R \cdot \frac{bd}{ad}.$$

The ratio of the resistances *ad* and *db*, with a wire of uniform material and thickness, is equal to the ratio of the lengths read on the scale.

(2) Calibration of the Bridge Wire

The continual movement of the sliding contact involves wear upon the measuring wire. The assumption made above of a uniform thickness of the whole wire is therefore usually not allowable, so that the measuring wire must first be calibrated. This is done by substituting a known resistance for $bc = W$ as well as for R. A calibration is made every 10 cm. from

10 cm. to 90 cm., and also every cm. from 95 to 99 cm. (the latter range is required later for the measurement of the resistance of the conductivity water). The calibration can easily be made with a single resistance box, if the box is arranged so that with a total resistance of 1000 ohm the resistance from 0 to 900 is in 100 Ω coils, and from 900 to 1000 in 10 Ω coils. If a resistance box of this kind is not available, then two sets of resistances must be used. For very accurate measurements the resistance box should be calibrated by comparison with a "normal resistance," but for ordinary work it can be assumed to be correct.

Every measurement is carried out three times. When repeating a reading, it is better not to look at the setting, to avoid any risk of self-deception. To avoid being disturbed by the hum of the induction coil, it is placed in a wooden box on a layer of felt, the box being kept closed during the measurement. It is very convenient to use a pair of telephones so that both ears are covered; they must be of low resistance (10 to 12 ohms).

The induction coil is only switched on during the actual measurement; otherwise the accumulator is too rapidly run down. If, on switching on, the buzzer does not start at once, the contact piece should be set vibrating by touching it carefully with a small pointed object (match or pencil point). If this does not succeed, the setting of the contact screw must be altered. It often happens that at a certain setting of the sliding contact the sound in the telephone suddenly (instead of, as though for a minimum, gradually at first) becomes weaker. There is, then a bad contact. This is usually to be got over by rubbing the place in question on the bridge wire with filter paper, whereby a layer of oxide is removed. *It must not be scratched or scraped with anything metallic, especially not with the knife-edge of the sliding contact pressed down hard.* For other difficulties, see page 162.

All wire connexions should be placed so as to be easily seen, and so that crossing of one wire by another is avoided as far as possible. Particular care should be taken that badly insulated wires do not lie alongside each other. (With alternating current measurements, rolling up wires which are too long is to be avoided because of the self-induction produced.) All terminals must be tightened and the ends of the wires to be connected must be scraped with a knife. Bad agreement of the measurements almost always arises from bad or shaky contacts.

The circuit used should be accurately sketched. The observations are to be entered in a table giving the two resistances unplugged and the corresponding bridge wire setting. The mean of the three readings taken at each place is taken as the setting. The measurements are used to draw up a table of corrections giving the number of mm. by which the setting as directly read is to be altered in order to obtain the ratio corresponding to the resistances unplugged. Care is to be taken about the correct sign: e.g. with a ratio of resistances 200 : 800 and a setting of 198·5, the correction to this setting is + 1·5 mm., since 1·5 mm. must be added to the value determined on the bridge wire, in order to obtain the value which corresponds to the actual ratio of resistance.

The corrections are also plotted graphically, corrections as ordinates against distances along the wire as abscissæ. Since in general a uniform alteration of the wire can be assumed over small intervals, the graph can be used to interpolate for the correction to settings lying between the calibrated points.

(3) Determination of the Cell Constant

For the theoretical significance of this quantity, see page 153. The determination of C is done by measuring the conductivity of a $^1/_{50}$ normal KCl solution, the specific conductance of which is 0·002765 reciprocal ohms at 25·0°, according to the accurate measurements of Kohlrausch. The solution is prepared from analytically pure KCl, dried at 300° and kept in a desiccator over pure sulphuric acid. Of this salt 0·3727 gm. is weighed out with brass weights in air, and dissolved in water at 18° in a 250 c.c. flask. "Conductivity" water is used (water which has been twice distilled, and which is kept guarded from atmospheric carbon dioxide by means of a soda-lime tube). A large store of this conductivity water should be prepared, so that all measurements may be made with the same water, the actual conductivity of which is determined (cf. 4) and applied as a correction. It is stored in a 1 litre flask with a two-hole stopper. Through one of these a syphon tube passes, and through the other projects the end of a soda-lime tube. The flask is filled, after first drawing CO_2-free air through for some time (attaching the syphon tube to the suction pump), by removing the syphon tube and introducing the delivery tube of the distillation apparatus, replacing the syphon tube when the water is in; by making the exchange of the two tubes quickly and carefully the amount of air containing CO_2 which gets in will be too small to be objectionable.

All vessels (the conductivity vessel, measuring flasks, storage flasks for conductivity water, pipettes) before being used must be repeatedly rinsed out with distilled water, steamed out for at least ten minutes, and then rinsed out again with conductivity water.

The KCl solution is introduced into the Arrhenius conductivity cell (Fig. 50) (cleaned as described and dried in the oven) to a level about 1 cm. above the narrow portion. The ebonite cover with the platinised platinum electrodes should not be put in the drying oven, since this would melt the cement (picein) with which the glass tubes are fixed in the cover. The electrodes and glass tubes are dried, after several rinsings with distilled water and conductivity water, by dipping them in pure absolute alcohol, and moving them quickly to and fro inside the drying oven for a short time.

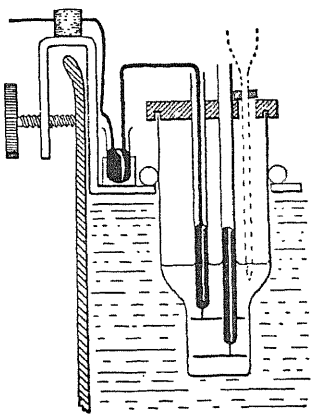

FIG. 50.

The conductivity cell, when filled, is held in the thermostat by means of the holder (see Fig. 50) so that it dips in to the extent of three-quarters. The temperature should be regulated exactly to 25·0°, and checked from time to time (see p. 3). The solution requires at least ten minutes to reach the thermostat temperature. In connexion with preserving the temperature constancy, one should avoid carrying on a measurement for too long a time without a break, otherwise the joule heat developed in the liquid by the passage of the current can produce a considerable rise in temperature. The scheme of connexions for the measurement is given in Fig. 49. Before the measurement it should be confirmed that the two glass tubes into which the electrodes are fused contain sufficient mercury, so that the connecting wires actually dip in; likewise the two mercury cups attached to the holder of the conductivity cell, which provide a means of connexion to the connecting wires free from strain, must be filled.

When all is ready, a definite resistance is unplugged (chosen so that the setting is not too near the end of the measuring wire, cf. p. 3 (5)) and the position of sound minimum is found. The setting is taken three times independently, and then the measurement is repeated with two other resistances unplugged.

The KCl filling of the cell is then renewed, and the series of measurements repeated. The filling must be renewed again, and until two consecutive fillings give, with the same comparison resistance, settings agreeing to within 1 mm.

A sketch of the connexions is made, and all the numerical results obtained are recorded in the following table :—

	Resistance unplugged.	Bridge wire setting.	Average.	Average Corr.	Temp.	Resistance.
1. Filling.	*a*	....	....	....	....	....
	b	....	....	....	....	....
	c	....	....	....	....	....
2. Filling	*a* *b* *c*					
3. Filling	etc.					

Using the average values corrected by the calibration of the bridge wire, the resistance of the KCl solution is calculated from each of the three settings. The average of all these values is taken, and substituted in the equation

$$C = 0{\cdot}002765 \times \text{mean resistance.}$$

Once the value of C has been determined great caution must be exercised not to alter the relative position of the two electrodes in any way. When taking out and putting in the electrodes they must not be rubbed against the sides of the conductivity cell or of the small conical flask. After the series of measurements the value of C should be checked with 0·02N KCl.

Note.—Difficulties in Conductivity Measurements

(*a*) The telephone is silent for all positions of the sliding contact. If the induction coil is working, the telephone is connected directly to the terminals of the secondary winding. If it then sounds, the cause of the previous silence must have been a broken contact (a wire badly connected to a terminal, or a loose contact). If it does not sound, there must be a break in the connexions or inside the telephone.

(*b*) A minimum cannot be found anywhere. If no mistake can be found, there must be a broken circuit in one of the arms. This is looked for as follows: first a connexion in the arm containing the conductivity cell is broken deliberately, whilst listening in the telephone; this is then reconnected and the circuit in the other arm, containing the resistance box, is broken. If in one case the telephone becomes completely silent, this shows that the

circuit in this arm, which had previously been intact, has now been interrupted. The fault must therefore lie in the other arm, the deliberate interruption of which is naturally without influence upon the telephone, since it was already interrupted. Usually the fault lies at one of the mercury contacts on the conductivity cell; apart from this it can only be a broken wire.

(*c*) The minimum is very indistinct. The cause is usually that the electrodes are not satisfactorily wetted, because of a partial covering with grease. (Avoid touching the electrodes with the fingers.) In this case the measurement can often be carried out satisfactorily by making a setting on the right and the left of the minimum at equal loudness, and taking the mean of the two values as representing the minimum. If, however, the results do not agree well, it becomes necessary to clean the electrodes thoroughly with sulphuric and dichromic acids and to replatinise.

Platinising the Electrodes.—The directions given in Ostwald-Luther, "Hand und Hilfsbuch zur Ausführung physiko-chemischer Messungen," are as follows: the platinising solution consists of 3 gms. chloroplatinic acid, 0·02 to 0·03 gm. lead acetate (or an approximately equal quantity of formic acid) and 100 gms. water. The electrolysing current, from two accumulators in series, is regulated to give a moderate gas evolution. The current is periodically reversed, so that each electrode serves as anode and cathode. The first platinising requires from ten to fifteen minutes; for replatinising electrodes already covered with platinum black one or two minutes is usually sufficient. The electrodes should be inclined to facilitate escape of gas, otherwise they become irregularly coated. To remove residual traces of the platinising solution, the electrodes are connected together as a cathode, and introduced together with a third platinum electrode as anode, into dilute sulphuric acid; on passing a current, any adsorbed chlorine is reduced to hydrochloric acid, which is comparatively easily washed away.

(4) Determination of the Specific Conductance of the Conductivity Water Used

The conductivity still shown by even the very purest water arises from the slight dissociation into $H^{\cdot}$ and OH'. Traces of electrolytes, particularly dissolved CO_2 from the air, increase the conductivity many-fold. The measurement of the conductivity of the water used is carried out just as already described for the conductivity of $\frac{N}{50}$ KCl solution. The conductivity cell is thoroughly rinsed out with distilled water several times, steamed out for ten minutes, and again rinsed out several times with the conductivity water. The electrodes are again carefully cleaned, and without previous drying, set in the conductivity cell in the thermostat. Since the resistance to be measured is now very high, the whole of the comparison resistance available in the box should be used. The filling must be renewed as often as is necessary, until two consecutive fillings show agreement to within 5 to 10 per cent. This small degree of accuracy is usually sufficient, since the value obtained is only used as a correction.

(5) Determination of the Molar Conductance of an Organic Acid

The organic acid, in calculated amount, is weighed exactly on an analytical balance, and dissolved in a 100 c.c. measuring flask. The initial concentration should in general be $\frac{N}{16}$, when the solubility permits. If the substance does not dissolve easily it should be warmed slightly on the water-bath and made up to the mark after cooling. Exactly 20 c.c. of the solution is pipetted by means of calibrated delivery pipette into the conductivity cell in the thermostat (the cell having been cleaned and dried). The electrodes are then put in, taking care to avoid air bubbles between the electrodes, and rubbing the latter against the walls.

After waiting ten minutes for temperature equalisation, a measurement is made, three times each with three different resistances, as described for the KCl solution. Then with a pipette calibrated for withdrawal 10 c.c. of the solution is removed, and with a delivery pipette 10 c.c. of conductivity water (warmed in the thermostat) is added. For this dilution the cover of the conductivity cell is not removed, the pipette being introduced through the hole. The position on the withdrawal pipette up to which it can be introduced without coming in contact with the upper electrode is marked with a small ring of rubber tubing. The delivery pipette is not dipped into the liquid in the conductivity cell at all. After adding the water it is carefully stirred through with the electrodes, by raising the cover, without touching the side walls or enclosing air bubbles in the process. After temperature equalisation the new resistance is determined exactly as before, with three different resistances unplugged. Another 10 c.c. is removed, and replaced by 10 c.c. of conductivity water as in the previous dilution. The measurements and dilutions are continued until an acid concentration of 1 mol in 1024 litres is reached. As far as possible the measurements should be carried out directly one after the other. All data should be entered in a table similar to the one given for the KCl measurements. The thermostat temperature should be checked from time to time and recorded.

(6) Calculation of Results.

The mean is taken of the three resistances measured at each dilution, and substituted in the equation

$$\text{spec. conductance } \chi = \frac{C}{\text{Measured resistance}}.$$

From the value obtained, half the specific conductance of the conductivity water is subtracted.[1] From the corrected specific conductances the molar conductances at the different concentrations are calculated by multiplication by the volume in c.c. containing 1 mol. From the composition of the acid the number of atoms is reckoned, and the value of Λ_∞ is taken from the table on page 155. From the ratios $\frac{\Lambda_v}{\Lambda_\infty}$, γ is found for the different concentrations. Finally the different values of γ and V are substituted in formula (71). Notice that here there is the difference from the earlier calculation, that V is to be calculated in litres. From the affinity constants obtained, the mean is taken, and multiplied by 100.

B. CONDUCTIMETRIC TITRATION

(a) Theory

This method, in which the minimum conductivity serves to indicate the equivalence point, is applicable when one kind of ion is replaced during the titration by another having a different migration velocity, as is particularly the case in the neutralisation of acids and alkalis. Thus in the titration of HCl with NaOH the OH′ ions of the added alkali combine with the very mobile $H^\cdot$ ions of the hydrochloric acid to form undissociated water, replacing them by the slow $Na^\cdot$ ions. (Equivalent conductance of $H^\cdot$ ions 315 Ω^{-1}, of $Na^\cdot$ ions 43 Ω^{-1}.) As the neutralisation proceeds the replacement becomes more complete and the conductivity sinks, until at the equivalence point there is a neutral solution of NaCl. If this point is overstepped by further

[1] The conductance of the water used for dilution, amounting to *ca.* $2 . 10^{-6}\ \Omega^{-1}$, is much greater than the true conductance of the purest water ($3{\cdot}8 \times 10^{-8}\ \Omega^{-1}$ at 18°) and does not, therefore, arise from the dissociation of water into $H^\cdot$ and OH′, but from some impurity. Since the acid used can effect the conductivity of such impurities to an extent depending upon their nature (with NH_3 for example, there would be salt formation with a decrease in total conductivity) it is difficult, in the absence of definite knowledge about the impurities, to know what kind of correction to make. Usually it is a trace of carbonic acid, the dissociation of which is repressed by the acid, in accordance with the law of mass action. It is, therefore, often recommended that half the conductance of the diluting water should be subtracted. In any case this uncertainty makes it essential in conductivity measurements to use no water which has a conductivity of its own comparable with that of the solution to be measured.

addition of alkali, the excess $Na^{\cdot}$ ions, and especially the mobile OH' ions (equivalent conductance = 174 Ω^{-1} cm.^{2}) come into action and the conductivity rises again.[1] Hence the conductivity minimum shows the neutral point. The phenomenon is only as simple as this in the case of strong acids and bases, and only in this case is a sharp break obtained. When titrating together acids and bases which are weak, or of different strengths, the phenomena are so complicated that a clear statement of the relationship between equivalence point and break in the conductivity curve cannot be given. Often there is only a flat minimum without a sharp break.

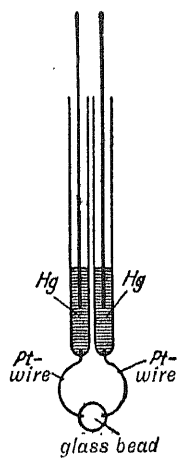

FIG. 51.

(b) Experimental

The general arrangement and method corresponds to that described for conductivity measurements. For the electrodes two platinum wires at any fixed distance are used. For example, they can be fused into two parallel glass tubes which are held together firmly by a rubber band, the ends of the wires being fastened by being fused into a glass bead (Fig. 51). The wires are platinised like conductivity electrodes (see p. 163). Since only relative measurements are made, the resistance constant need not be determined; it is only necessary that it should remain constant throughout the measurement. A large glass beaker containing the liquid to be titrated serves as the conductivity cell, and stands in a thermostat. The acid or alkali of known normality is run out of the burette a c.c. at a time, well stirred, and allowed to reach temperature equilibrium (*ca.* three to five minutes). The resistance is then measured. Each time the number of c.c. of added acid or alkali, and the position of the sliding contact for sound minimum, are noted. If a constant comparison resistance is used throughout the whole measurement, these two sets of values can be used directly for constructing a diagram: ordinates: bridge settings; ab-

[1] Superimposed upon the effect on the conductivity due to ions of different velocities is the decrease in specific conductance due to increasing dilution; this, however, takes place continuously (without any sharp break). If the arrangement of electrodes were such that with a constant width and distance apart the whole depth of the electrolyte fell between the electrodes all the time, this effect would not exist.

scissæ: number of c.c. added; from this the discontinuity in the curve, and hence the number of c.c. required for neutralisation is found. If different comparison resistances are used, the resistance of the solution must be calculated every time, and plotted in the diagram against the number of c.c.

Reference:—
H. S. Taylor. Chap. XIII, pp. 854-60.

XVI. TRANSPORT NUMBERS

A. THE TRANSPORT NUMBER OF THE $Ag^{\cdot}$ ION IN A SOLUTION OF $AgNO_3$

(a) Theory

(1) THE current carried by an electrolyte is made up of the parts carried by the separate ions (cf. formula 61). The fraction of the total current carried by one kind of ion is called the "transport number" of the ion in question (Hittorf). It represents the ratio of the conductance of this ion to the total conductance of the whole electrolyte. Formula (62) gives for the transport number of an ion in a binary, uni-univalent electrolyte (where both ions have the same valency and concentration):

$$n_k = \frac{u}{u+v}; \quad n_a = \frac{v}{u+v} \quad . \quad . \quad . \quad (74)$$

From (74) the relationship follows (true also for an electrolyte which is not uni-univalent) that the transport numbers of anion and cation together add up to 1:

$$n_k + n_a = 1; \quad n_a = 1 - n_k. \quad . \quad . \quad (75)$$

(2) The experimental determination of a transport number involves a study of the changes in concentration taking place in the neighbourhood of the electrodes. Suppose that $1F = 96{,}494$ coulombs is passed through a $AgNO_3$ solution between silver electrodes, the following processes take place:

(α) At the cathode, where the negative current enters, one equivalent of $Ag^{\cdot}$ is discharged from the solution and precipitated on the electrode in the form of neutral metallic silver.

In the solution the current is carried by the moving ions, and is divided between the two kinds of ions in the ratio of their mobilities. Hence, of the total amount of electricity $1F$, $\frac{u}{u+v}$. F is carried by the $Ag^{\cdot}$ ions into the cathode space,

and $\frac{v}{u+v}$. F by the NO_3' into the anode space. Thus whilst from the cathode liquid 1 gm. equivalent positive $Ag^{\cdot}$ disappears by discharge, simultaneously $\frac{u}{u+v}$ gm. equivalents $Ag^{\cdot}$ migrate to it, so that *the change in the total amount of* $Ag^{\cdot}$ *in the cathode space* amounts to $-1+\frac{u}{u+v}=\frac{-v}{u+v}$ gm. equivalents; there is a disappearance of $\frac{v}{u+v}$ gm. equivalents of $Ag^{\cdot}$. The solution, however, remains electrically neutral, because in the same time $\frac{v}{u+v}$ gm. equivalents of NO_3' migrate out of the cathode liquid.

(β) At the anode there is the corresponding process: through the removal of 1F electrons 1 gm. equivalent of positively charged $Ag^{\cdot}$ ions is formed from 1 equivalent of neutral silver, and passes into the solution. At the same time $\frac{u}{u+v}$ gm. equivalents of $Ag^{\cdot}$ migrates out of the anode space, so that here the *total change* is $+1-\frac{u}{u+v}=+\frac{v}{u+v}$ gm. equivalents of $Ag^{\cdot}$. Since $\frac{v}{u+v}$ gm. equivalents of NO_3' migrate in, the solution remains electrically neutral here also.

Reviewing the complete change, it appears that by the passage of 1F there is a decrease of $\frac{v}{u+v}$ mol of $AgNO_3$ in the cathode space, and an equally great increase in the anode space. Thus the determination of the concentration change, either round the cathode or round the anode, affords a means of measuring the transport number of the anion.

(3) Suppose that in an actual experiment, in which the liquid in the anode space is to be analysed, an accurately known quantity of electricity, say c . F coulombs, is passed through the electrolysis cell, then in the anode space c gm. equivalents of $Ag^{\cdot}$ are formed. If there were originally in the whole of the space round the anode in which change of concentration takes place, a gm. equivalents of $Ag^{\cdot}$ (determined by titration of a weighed amount of the anode liquid), and if during the experiment x gm. equivalents migrate away, then after the experiment a new titration of the anode liquid gives the final amount $b=a+c-x$; or $x=a+c-b$. The transport

number of $Ag^{\cdot}$ is then found as the ratio of the quantity of electricity carried by the x gm. equivalents, to the total quantity of electricity which has passed through; the latter, measured in current equivalents (F) is identical with c, the number of equivalents of $Ag^{\cdot}$ produced by anodic solution. The transport number of $Ag^{\cdot}$ is therefore

$$n_{Ag^{\cdot}} = \frac{x}{c} = \frac{a + c - b}{c} = \frac{a - b}{c} + 1 = 1 - \frac{b - a}{c},$$

and that of NO_3' must be $n_{NO_3'} = \frac{b - a}{c}$. This agrees with the previous consideration of the processes in the cathode and anode spaces; there the result was obtained that through the passage of 1F the quantity of $AgNO_3$ in the anode space increases by $\frac{v}{u + v}$. Since now c . F passes, the increase found is $b - a = \frac{v}{u + v} . c$ mols, or the transport number of NO_3' is

$$\frac{v}{u + v} = \frac{b - a}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

References :—

Eucken, Jette, and Lamer. § 246.
Nernst. Bk. II, Chap. VIII, pp. 414-30. Chap. IX, pp. 460-64.
H. S. Taylor. Chap. XI.

(b) Experimental

The concentration change in the anode layer is measured by means of a special transport apparatus (cf. Fig. 55) which allows the anode layer to be separated conveniently from the rest of the electrolyte. The quantity of electricity passed through is determined in three different ways, as a check: by a copper coulombmeter, a silver titration coulombmeter, and by calculation from the current strength and the duration of the experiment.

(1) Measurement of the Quantity of Electricity

(α) *Copper Coulombmeter.*—This has two electrodes of thin copper sheet, fastened to a wooden cover by means of screw terminals. The wide surface of the electrodes is joined at the top to a narrow strip-shaped stem (Fig. 52) which passes through the surface of the electrolyte making a narrow zone of contact, so as to expose as small a fraction as possible of the freshly

precipitated copper to oxidation by atmospheric oxygen. The cover fits on to a glass beaker, which is filled three-quarters full with the electrolysis liquid. The increase in weight of the cathode is determined. Before the experiment *the cathode must be freshly electro-plated with copper* (which is done simultaneously with the silvering described under (2)). After passing the current, both when electro-plating and in the actual measurement, it is rinsed twice with distilled water and then with absolute alcohol, and dried quickly in the oven by moving it to and fro. It is then weighed on the analytical balance accurately to $^1/_{10}$ mg. For the electrolysis liquid "Öttel's solution" is used, which contains 150 gms. $CuSO_4 . 5H_2O$, 50 gms. concentrated H_2SO_4 and 50 gms. alcohol per litre. During the measurement hydrogen is led in through a tube passing through the cover and bubbles through the liquid; this serves both to stir the electrolysis liquid well, so preventing impoverishment of the cathode layer in $Cu^{\cdot\cdot}$ ions, and to keep away atmospheric oxygen to a considerable extent, which readily oxidises the fresh copper precipitate. Because of this tendency to oxidise, drying at a high temperature is to be avoided (*not over an open flame*). The dried precipitate should be uniformly bright red, without dull blackish places; otherwise oxide formation has taken place and the weight will be too high. The number of current equivalents passed is found by dividing the weight of the deposit, in gm., by 31·785, the equivalent weight of copper.

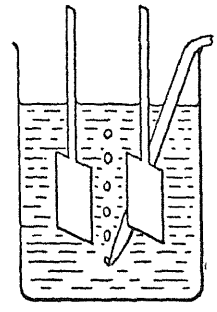

FIG. 52.

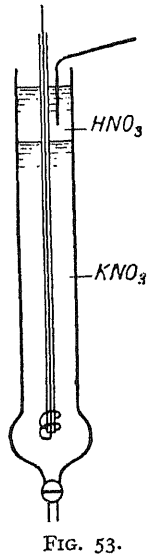

FIG. 53.

(β) *The Silver Titration Coulombmeter.*—This consists of a glass tube about 30 cm. long, widened into a bulb at the lower end, which carries an exit tube with a tap (Fig. 53). A silver electrode is introduced (for its preparation see p. 202) so that the silver wire is in the bulb. The coulombmeter is filled with *halogen-free* 15 to 20 per cent. KNO_3 or $NaNO_3$ solution up to about 5 cm. from the top, and over this a layer of 0·5N HNO_3 is put cautiously. A platinum wire in the nitric acid serves as the place of entry of the negative current (cathode). After the experiment the solution is run

out, so far only that the nitric acid does not come into contact with the silver, and the dissolved silver is titrated in the usual way with 0·1N KCNS and ferric ammonium alum as indicator.

(2) Silvering the Electrodes

Before every measurement the silver electrodes to be used in the titration coulombmeter and the transport apparatus are freshly silvered, so that the surface is clean, and a gradual using up of the electrodes is avoided. For this purpose the two electrodes which are later to be used as anodes are connected up as cathodes (see Fig. 54 for the scheme of connexions). The silvering is done in a small glass beaker. The anode is a small lump of silver, half-immersed in the liquid, and attached to a silver wire; in this way the corrosion of the silver connecting wire is avoided. The brass connecting clamp to which the silver wire leading to the anode is attached must not dip in the silvering solution, otherwise the latter will be made unusable

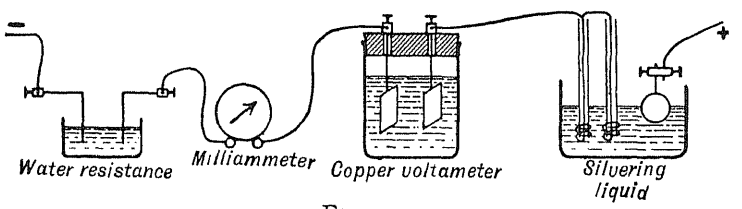

Fig. 54.

by the anodic solution of Zn and Cu. The silvering solution is made up according to the following recipe: 1·3 gm. of pure $AgNO_3$ is dissolved in a few c.c. distilled water, and treated with a concentrated solution of the *purest* KCN (failures with the silvering are usually caused by the use of impure KCN) drop by drop until the white precipitate of AgCN is just dissolved. It is then made up to 50 c.c. As long as the silvering liquid is not contaminated with any foreign metal, it can always be used again. After use it is poured back into the stock flask, not into the silver residues.

The silvering is done with a current strength of 6 to 8 milliamps. during at least ten hours. The 110-volt main leads serve as a source of current; the current is regulated by a water resistance filled with distilled water, and to which a few drops of conducting liquid are added, as required. The silver coating on the electrodes must be quite uniform and fine-grained, and must remain firmly attached when being washed. Loose

precipitates, easily recognised by their coarse grain and spongy condition, are due either to too high a current strength, or most often to impurities in the silvering solution.

(3) The Transport Apparatus

A transport apparatus of the form shown in Fig. 55 is used. The solution used in it is about 0·05N $AgNO_3$. The exact content of the solution is ascertained before beginning the experiment by titrating a weighed quantity. The left limb, with the exit tube is filled with this solution up to the horizontal connecting tube. The other limb is filled about 6 cm. deep with saturated $Cu(NO_3)_2$ solution. Over this the approximately 0·05N $AgNO_3$ solution is poured, in the following manner: a suitable round cork disc (which, for its more convenient removal later, carries a match stuck into the upper side as a shaft) is made to float on the $Cu(NO_3)_2$ solution, and the $AgNO_3$ solution is allowed to flow slowly from a pipette on to this floating disc of cork. This gives a sharp boundary between the two solutions. $AgNO_3$ solution is introduced until the horizontal connecting tube is filled completely. The copper cathode is now introduced into the limb on the right, beneath the $Cu(NO_3)_2$, and the freshly silvered silver anode into the limb on the left, to a depth such that the electrode is within the bulb-shaped enlargement (Fig. 56). The electrodes are then connected to the other measuring apparatus as in Fig. 56—the copper coulombmeter, the silver titration coulombmeter, and the milliammeter, and then to the 110-volt main leads (having previously determined the poles of the latter (cf. p. 148)). With the concentrations given and the usual apparatus dimensions the strength of current

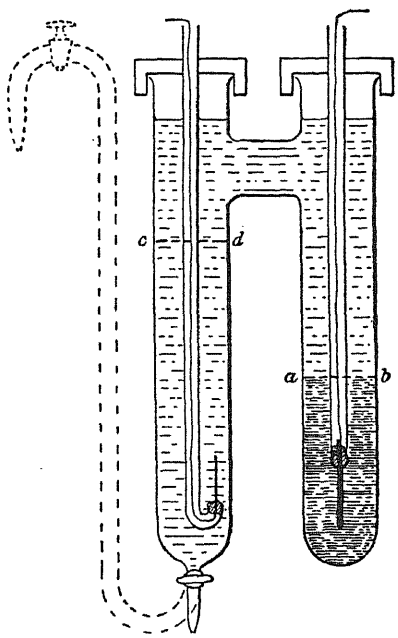

Fig. 55.—Transport apparatus.

produced will be about 10 milliamps. Duration of experiment: two hours. Before switching on the circuit should be checked over carefully.

At the end of the experiment the anode layer is let down until the level of the solution is about 1 cm. above the bulb-shaped enlargement. Experience shows that under these experimental conditions the whole of the layer in which any change has taken place is secured. (The equivalent conductance of $Ag^{\cdot}$ at 18° is 54·3 Ω^{-1}. The absolute velocity of migration is therefore in a field of 1 volt/cm. $\frac{54{\cdot}3}{96494}$ cm./sec. [cf. (70), p. 155]; with the experimental arrangement used the field amounts to

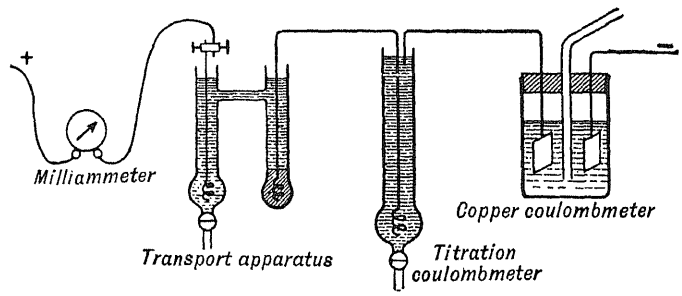

FIG. 56.—Arrangement for measuring the transport number of $Ag^{\cdot}$ ion.

about 1·5 volts/cm., the migration velocity being therefore $\frac{54{\cdot}3 \times 1{\cdot}5}{96494} = 0{\cdot}00084$ cm./sec. In two hours the $Ag^{\cdot}$ ions move $7200 \times 0{\cdot}00084$ cm. = *ca.* 6·0 cm. Hence the change in concentration reaches as far as this, reckoned from the electrode. It is necessary, therefore, to run off a column of liquid of at least this length, measured from the upper edge of the silver wire.) The anode liquid run off is weighed accurately to $^1/_{100}$ gm. (= n gm.) and its content of silver titrated with $\frac{N}{10}$ KCNS and ferric alum, according to Volhard, or with $\frac{N}{10}$ KBr and Rhodamin 6 G.[1]

This gives the number of gm. $AgNO_3$ (= b gm.), which are contained in $(n - b)$ gm. of water. Similarly, the titration of the original solution gives the number of gm. $AgNO_3$ which

[1] According to K. Fajans and Wolff, *Z. f. anorg. allg. Chemie*, **137** (1924), p. 221. Cf. J. M. Kolthoff: "Die Massanalyse," Part I (1927), p. 104, and Part II (1928), p. 235.

were contained in a definite weight of water before the transport [m gm. solution: containing, according to the titration d gm. $AgNO_3$ to $(m - d)$ gm. water]. Hence in $n - b$ gm. of water there were originally $\frac{d(n-b)}{m-d}$ gm. $AgNO_3 = a$ gm. $AgNO_3$. The increase $b - a$, divided by the quantity of $AgNO_3$ produced by anodic solution in the titration coulombmeter ($= c$ gm.), gives the transport number of the anion $\frac{b-a}{c}$ (cf. p. 170).

The data of the copper coulombmeter must agree with those of the titration coulombmeter within $\frac{1}{2}$ to 1 per cent. If the discrepancy exceeds this the experiment is useless and must be repeated. The mean of the two results is taken, giving the value from the titration coulombmeter double weight. The quantity of electricity calculated from the current strength and the duration of the experiment only agrees well with the results of the coulombmeters when there have been no fluctuations in the current. In order to obtain an exact value when there are fluctuations, they have to be exactly followed. In general, a reasonable value is obtained by reading the current strength every five minutes, and taking the mean.

The $AgNO_3$ solution is poured into the residues bottle. The $Cu(NO_3)_2$ solution, which during the experiment becomes contaminated with $AgNO_3$, is thrown away. The copper electrodes of the copper coulombmeter and of the transport apparatus are well rinsed with water and dried with absolute alcohol.

B. TRANSPORT NUMBER OF HYDROGEN ION IN DILUTE SULPHURIC ACID

(a) Theory

If $\frac{N}{100}$ H_2SO_4 is electrolysed between two clean lead electrodes, only the cathode process is exactly defined; it consists of the discharge of $H^{\cdot}$ with formation of gaseous hydrogen. At the anode, on the other hand, according to the experimental conditions, both OH' and SO_4'' are discharged, with formation of oxygen or $PbSO_4$. Definite results can therefore only be obtained by the experimental investigation of the process taking place in the cathode space.

Suppose that 1F is allowed to flow through the cell: at the cathode 1 gm. equivalent of $H^{\cdot}$ is discharged; at the same time

$\frac{u}{u+v}$ equivalents of $H^{\cdot}$ migrate out of the anode space and into the cathode space, and $\frac{v}{u+v}$ equivalents of SO_4'' out of the cathode space into the anode space, where u is the migration velocity of the $H^{\cdot}$ and v is one-half the migration velocity of SO_4''. The total alteration of concentration in the cathode space is therefore $-1 + \frac{u}{u+v} = -\frac{v}{u+v}$ equivalents of $H^{\cdot}$; and since at the same time $\frac{v}{u+v}$ equivalents of SO_4'' migrate away, the solution remains electrically neutral. From this measurable alteration in H_2SO_4 concentration in the cathode space the transport number of the anion and therefore also of the cation can be determined.

(b) Experimental

About 1 litre of *ca.* $\frac{N}{100}$ H_2SO_4 is prepared; the acid need not be exactly $\frac{N}{100}$ but its titre must be exactly determined by titration of a weighed amount with $\frac{N}{10}$ NaOH and methyl-orange as indicator. Two glass beakers are then filled to a depth of about 10 cm. with this acid, and connected together by means of a U-shaped syphon tube. The syphon is fitted on top with a T-piece, a short length of rubber tube and a clip, so that it can be filled with acid by suction. The beaker which is to serve as cathode vessel must first be weighed accurately to 0·1 gm. In the glass beakers are two 1 mm. thick lead plates, 7 × 10 cm., which act as electrodes. The cathode must first be made bright with emery paper. The copper and the silver titration coulombmeters (for setting these up, see p. 170), the milliammeter and the transport apparatus are connected in series, without a water resistance, to the 220 volt leads, and a current of 50 milliamps is allowed to flow for one hour. The circuit is shown in Fig. 57.

The current heats the contents of the syphon, and the warmth produced in the part of it which does not dip in makes the liquid a little lighter and so hinders mixing of the contents of the two vessels by convection. To make this heating sufficiently strong, the current should not be weaker than that stated; sulphate formation at the cathode is also hindered thereby. After one

hour the current is cut off, the clip opened and the contents of the syphon allowed to flow into the two vessels. The syphon and the cathode are then taken out and allowed to drip into the cathode vessel, without washing. The contents of the cathode vessel are weighed to 0·1 gm. Titration with $\frac{N}{10}$ NaOH gives the mol content of $H^{\cdot}$ after the transport (= b mol). Because of the great dilution of the acid and the small change in concentration taking place during the experiment, it is not here necessary, as it was with $AgNO_3$, that the acid content should be referred to the same quantity of water. From the titre of the original acid the number of mols of $H^{\cdot}$ (= a mols) contained in the weighed quantity of acid before the experiment is calculated

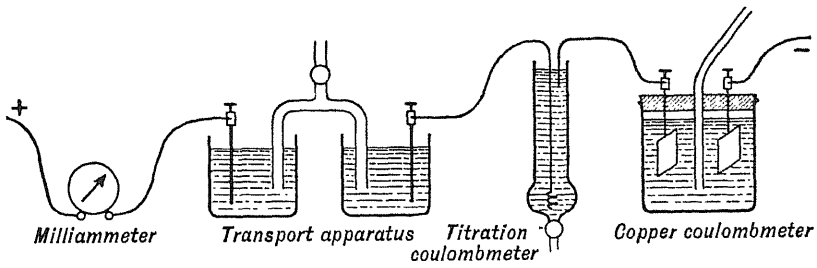

FIG. 57.—Arrangement for the measurement of the transport number of $H^{\cdot}$ ion.

If the quantity of electricity passed (calculated from the data of the coulombmeters) corresponds to a deposition of c mols $H^{\cdot}$, then had there been no migration in of $H^{\cdot}$ the $H^{\cdot}$ content would have become $a - c$ mols. Hence $b - (a - c)$ mols have migrated in. The transport number of $H^{\cdot}$ is therefore

$$n_{H^{\cdot}} = \frac{b - a + c}{c} = 1 - \frac{a - b}{c};$$

that of $\frac{1}{2}SO_4''$ is accordingly $\frac{a - b}{c}$.

With regard to the closeness of the agreement of the coulombmeter results, cf. page 175.

Note.—For the determination of the transport number in electrolytes containing Cl' (e.g. KCl, NaCl, NH_4Cl, $BaCl_2$ or HCl) the apparatus of Hopfgartner (*Z. physikal. Ch.*, **38**, 127) is very convenient. The anode is a well-amalgamated cadmium rod,

and the cathode mercury covered with a concentrated $ZnCl_2$ solution. The transport number is obtained from the increase of Cl′ concentration in the anode space, as determined by titration before and after the experiment. No cadmium should be detectable by $(NH_4)_2S$ in the middle layer. The amount of electricity passed is determined in a copper coulombmeter.

XVII. ELECTROMOTIVE FORCES

A. GENERAL PART

(a) Theory

(1) A GALVANIC cell provides a means of obtaining, in the form of electrical energy, the work which a *spontaneous* chemical or osmotic process can produce. If the cell works *reversibly*, the work obtained is the *maximum work* and is a measure of the *free energy* or the *affinity* of the process. Since the work A is equal to the product of the potential difference E and the quantity of electricity $n \cdot F(A = n \cdot E \cdot F)$, and the number of current equivalents $(n \cdot F)$ flowing for a definite change is ascertained quite easily, it follows that the free energy can be found by a measurement of the E.M.F.

(2) The complete process taking place in a galvanic cell during the passage of the current can be divided up into separate parts: thus in a Daniell cell, in which copper dips into copper sulphate and zinc into zinc sulphate, the *complete process* is

$$Zn + CuSO_4 = Cu + ZnSO_4$$

It consists of the following separate processes:—

(*a*) At the Zn electrode: metallic Zn dissolves with formation of $Zn^{\cdot\cdot}$, and giving up electrons: $Zn - 2 \ominus = Zn^{\cdot\cdot}$.

(*b*) At the Cu electrode: $Cu^{\cdot\cdot}$ ions take up electrons and deposit themselves as metallic copper: $Cu^{\cdot\cdot} + 2 \ominus = Cu$.

(*c*) In the solution SO_4'' migrates in the direction of the — stream out of the $CuSO_4$ solution into the $ZnSO_4$ solution. $Cu^{\cdot\cdot}$ and $Zn^{\cdot\cdot}$ ions migrate in the (opposite) direction of the + stream.

Analogously, the *total potential difference* of the element can be divided up into single potential differences corresponding to the partial processes. In the Daniell cell they are located where the Cu electrode is in contact with the $CuSO_4$ solution and where the Zn electrode is in contact with the $ZnSO_4$ solution ("Electrode potentials"), and in addition, at the place of contact between

the two solutions, where ions move from one solution into the other (" Liquid-liquid " or " diffusion " potentials).

The separate potentials can be referred to the absolute zero potential; in practice, however, they are referred to the *normal hydrogen electrode*, the potential of which is arbitrarily taken = 0. The normal hydrogen electrode consists of a platinised platinum plate, charged with hydrogen at 1 atm. pressure, and dipping in a 1N solution of $H^{\bullet}$ ions. The electrode of which the single potential is to be determined is combined with this normal hydrogen electrode to form a galvanic element, and the resulting potential is given the + sign when the electrode is + in this combination and the — sign when it forms the — pole.

The total potential difference of a galvanic cell is practically governed by the difference between the single potentials of the electrodes. In any case the direction of the current in the complete cell is determined by this potential difference. The diffusion potentials which have also to be taken into account are always merely quantities which come in as corrections, and have to be added or subtracted according to circumstances to the difference of the electrode potentials. It is important to take into account the signs of the single potentials. If, for example, the single potential of a Cu electrode in a $\frac{M}{1}$ $Cu^{\bullet\bullet}$ solution is + 0·34 volt, and that of a Zn electrode in $Zn^{\bullet\bullet}$ solution of the same concentration is — 0·76 volt, then the total potential difference of the cell $Cu/\frac{M}{1}Cu^{\bullet\bullet}/\frac{M}{1}Zn^{\bullet\bullet}/Zn$ (neglecting the liquid potential which in this case is vanishingly small) is $E = E_{Cu} - E_{Zn} = +0{\cdot}34 - (-0{\cdot}76) = 1{\cdot}10$ volt, the Cu electrode being positively charged with respect to the Zn to the extent of 1·10 volt. In exactly the same way the potential difference is found for a cell formed by combining two metals with positive single potentials; e.g.

$$Ag\Big/\frac{M}{1}Ag^{\bullet}\Big/\frac{M}{1}Cu^{\bullet\bullet}\Big/Cu.$$

Single potentials + 0·80 + 0·34

Total potential difference = + 0·80 — (+ 0·34) = + 0·46 volt. Ag is the + pole. The surest way of avoiding errors of sign is to make a diagrammatic representation (Fig. 58), drawing the single potentials as lines above or below a zero line representing the normal hydrogen potential, according to sign:

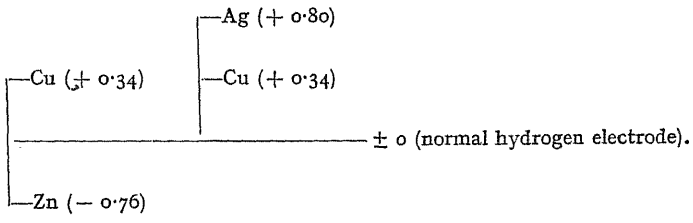

FIG. 58.

(3) The single potentials may themselves be resolved into two partial quantities: a quantity which is characteristic of the electrode—the "normal potential" which refers to the concentration $c = 1$ of the solution, and a second quantity which takes account of the concentration c of the solution into which the electrode dips. In the Nernst formula for the single potential this resolution appears in the form

$$\text{Single potential } E = \frac{RT}{\nu \,.\, F} \log_e \frac{1}{c_0} + \frac{RT}{\nu \,.\, F} \log_e c \,.$$

$$= \epsilon_h + \frac{RT}{\nu \,.\, F} \log_e c. \quad (77)$$

The quantity ν gives the number of elementary charges carried by the ion in the solution. If $c = 1$ the second term disappears, leaving a quantity characteristic of the metal in question, the normal potential. This is the potential, measured against the normal hydrogen electrode, to which an electrode becomes charged in a 1 molar solution of its ions, and is usually represented by ϵ_h. The meaning of c_0 is seen from the fact that $E = 0$ when $c = c_0$. Since the potential difference is imagined as caused by ions passing out of the metal into the solution (solution pressure), and vice-versa (deposition pressure = osmotic pressure), and $E = 0$ when the solution pressure is equal to the osmotic pressure, therefore c_0 is the concentration of electrolyte for which the osmotic pressure equals the solution pressure. The formula is deduced in the following way: in *one* arrangement the electrode is immersed directly in a solution of concentration $c (c_0 > c)$; under the potential difference $-E$, to which it becomes charged, 1 mol of positive ions is allowed to pass into the solution in a reversible manner (by opposing an electromotive force which is smaller by only an infinitesimal amount). In this way the electrical work $\nu \,.\, (-E) \,.\, F$ is obtained from the system. The amount of solution is chosen so large that its concentration and therefore also the potential E remains constant during the transfer.

In *a second* arrangement the electrode is immersed in a solution of concentration c_0, in which, as already stated, the osmotic pressure is equal to the solution pressure of the metal. Consequently there is no potential difference between electrode and solution, and 1 mol of ions can be transferred from the metal to the solution without expenditure of electrical energy. These ions are then expanded in an osmotic way isothermally and reversibly to the concentration c of the first solution. Thereby the osmotic work $RT \log_e \frac{c_0}{c}$ is obtained. The amounts of maximum work obtained in these two ways are equated: electrical work by the first way = osmotic work by the second way:

$$\nu \,.\, (-E) \,.\, F = RT \log_e \frac{c_0}{c} \quad \text{or} \quad \nu \,.\, E \,.\, F = RT \log_e \frac{c}{c_0}.$$

The formula gives the correct sign for the single potential of the metal electrode against the solution of its ions; in the case of an electrode which produces anions, e.g. iodine, the sign applies to the solution with respect to the electrode.

If the single potentials are written in the manner just described, the expression for the E.M.F. of a cell takes the form,

$$E = \epsilon_{h_1} + \frac{RT}{\nu_1 \,.\, F} \,.\, \log_e c_1 - \left(\epsilon_{h_2} + \frac{RT}{\nu_2 \,.\, F} \log_e c_2\right) \quad . \quad (78)$$

This is the most general formula, which is applicable to any galvanic cell in which the process producing the current consists of interchanges between chemical elements and their ions.

If E is measured in volts and F in coulombs, the electrical work is in joules or in watt-seconds. R must therefore also be expressed in joule/1°: R = 8·31 joule/1°. If the temperature is room temperature = 18° C. = 291° abs., and decimal logarithms are used instead of natural logarithms,

$$\frac{RT}{\nu \,.\, F} \log_e c = \frac{8{\cdot}31 \times 291}{\nu \,.\, 96494 \times 0{\cdot}4343} \,.\, \log_{10} c = \frac{0{\cdot}0577}{\nu} \log_{10} c.$$

The single potential of an electrode can then be more simply written in the form $\epsilon_h + \frac{0{\cdot}058}{\nu} \,.\, \log_{10} c$, from which it appears that by increasing the ion concentration by one power of 10, the potential of the electrode with respect to the solution (with univalent positive ions) becomes more positive by 0·058 volt, and with univalent negative ions (OH′; Cl′; Br′; I′) more

negative by the same amount. With divalent ions ($\nu = 2$) this change in concentration corresponds to a change in potential of 0·029 volt.

References :—

Eucken, Jette, and Lamer. §§ 207-18.
Nernst. Bk. IV, Chap. VII, Chap. VIII.
Le Blanc. Chap. VII.
H. S. Taylor. Chap. XII.
R. A. Lehfeldt. Electro-Chemistry. Longmans (1918), pp. 197, 235 (Capillary electrometer).

(b) Experimental

(1) The Method of Measurement

In the deduction of the formula for the single potential indicated on page 181, the osmotic and electrical work can only

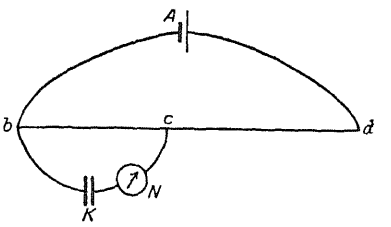

Fig. 59.

be equated if they represent *maximum* work, obtainable by carrying out the separate processes *reversibly* and isothermally. Also the concentration of the solution must remain practically constant when the ions are transferred from the electrode; for this reason, when the transfer of 1 mol of ions was considered, a very large volume of solution was chosen. But the conditions referred to can also be realised by allowing only a very small amount of change to take place in the cell during the measurement of E. This is the case when Poggendorf's compensation method is used, in which the E.M.F. of the cell to be measured is opposed by an equal E.M.F. applied externally, so that the cell is prevented from working. The ionic concentrations then remain unaltered. The arrangement is illustrated in Fig. 59: the potential difference of an accumulator A is allowed to fall along a measuring wire stretched along a scale. If the wire is uniform, the potential falls uniformly from one end to the other, and the ratio of the fall of potential from *b* to *c* to the total

potential fall from b to d is as the lengths $bc : bd$. (The measuring wire calibrated for the conductivity experiments can be used, with the corrections already determined.) Thus between the end b of the wire and a movable sliding contact c any potential difference can be accurately determined, provided it lies within the total potential difference. If a potential difference E′ is tapped off between b and c, and a galvanic cell K with E.M.F. E is connected in opposition to this (e.g. at b the + pole of the cell opposing the + pole of the accumulator) then if E is exact equal to E′, no current flows in the subsidiary circuit bKNc, as can be observed with a sensitive null instrument N (galvanometer or capillary electrometer). In the measuring wire there is, of course, a current flowing between b and c. If the sliding contact is moved a little to the left from this null position, E is greater than E′, and the cell K sends the negative current (electrons) in the direction bKNc in the subsidiary circuit. If the sliding contact is a little to the right of the null position, E′ is greater than E, and the accumulator A sends the negative current in the opposite direction cNKb. The element K behaves in the latter case like an electrolytic cell, and the whole process takes place as the reverse of the process in the first case, where it behaves as a galvanic cell. In the null position the force equals the opposing force. E is therefore measured with the working process carried out reversibly, and thus a real measure of the maximum work is obtained.

E could be measured in this way directly, if the E.M.F. of the accumulator were accurately known and remained constant for a long time. But since constancy is always obtained for a short time only, the accumulator must first be standardised, by determining its E.M.F. at the moment with a normal cell (see below). If a balance is obtained at the position f, the E.M.F. of the accumulator $E_a = E_n \cdot \frac{bd}{bf}$. Then between b and c the potential difference is $E_n \frac{bd}{bf} \cdot \frac{bc}{bd} = E_n \frac{bc}{bf}$. Every measurement of the galvanic cell K is done between two measurements of the normal cell. If the two settings for the normal cell do not differ by more than 2 mm., the average is taken. If, however, the setting for the normal cell alters by more than this amount in a few minutes, the accumulator is running down. With a quite freshly charged accumulator there are also quite large alterations of E.M.F. for the first few minutes during which current is taken from it. In this case the circuit Abd is closed for some time

and the measurements made after waiting about a quarter of an hour.

(2) Auxiliary Apparatus

(α) *The Cadmium Normal Cell.*—Fig. 60 shows the internal constitution of the cell, and a form of construction which has been found satisfactory, with Hg contacts [1] and glass feet. The process producing the current is

$$Cd + Hg_2SO_{4\,solid} = CdSO_{4\,solid} + 2Hg.$$

Hg is the positive, Cd the negative pole. In setting-up such a cell, the glass vessel is first cleaned with hot nitric acid, then washed with distilled water, steamed out for a quarter of an hour,

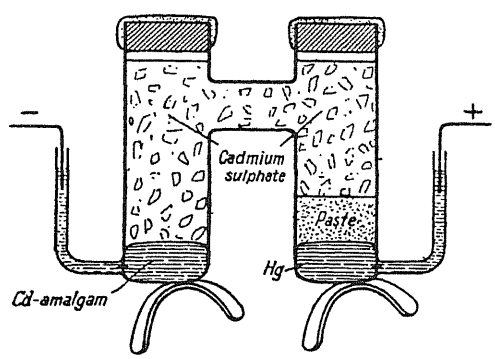

Fig. 60.

washed out with conductivity water, and dried. One limb contains cadmium amalgam, prepared by heating one part of the purest cadmium with seven parts of the purest distilled mercury. It is liquid at the temperature of the water-bath, and is introduced in this state to a depth of about $\frac{1}{2}$ cm. On cooling it solidifies. The other limb contains distilled mercury to about $\frac{1}{2}$ cm., and over this a paste of solid Hg_2SO_4, crushed crystals of $CdSO_4 . \frac{8}{3} H_2O$ and Hg, which is rubbed into a paste with saturated $CdSO_4$ solution. The paste must be so viscous that small crystals of cadmium sulphate can be poured on to it without sinking in to any considerable extent. Small crystals of $CdSO_4 . \frac{8}{3} H_2O$ are also put into the whole of the space above the cadmium amalgam, and the connecting tube between the two limbs. Finally a $CdSO_4$ solution saturated with these crystals

[1] The more usual *wire* contacts are apt to break with frequent use.

is poured in, and both limbs are closed by a layer of paraffin, and then by paraffined corks. A small bubble of air is left under the corks, otherwise the rise of temperature (during a hot summer) would cause the cell to burst. The outer ends of the corks are coated with sealing-wax. Electrical connexion is made through copper wires pushed into the small Hg-filled side tubes, from which platinum wires are fused through into the interior of the cell. A normal cell made as described reaches its correct E.M.F. in a short time, and even immediately after being prepared, differs by only a few tenths of a millivolt from the proper value.

The E.M.F. of the cadmium normal cell between 15° and 25° is given by

$$1{\cdot}0183 + 0{\cdot}00004\,(20^\circ - t^\circ) \text{ volts.}$$

With this arrangement for measurement, however, the accuracy is not greater than about 1 millivolt, so that the small temperature coefficient need not be taken into account.

(β) *Capillary Electrometer.*—The usual form is that devised originally by G. Lippmann and later improved by R. Luther (enclosed form (Fig. 61)). The use of this instrument as a null instrument depends upon the following facts: the surface tension of mercury in contact with dilute sulphuric acid varies with the extent to which the metal is charged relatively to the acid. Normally it is positively charged as a result of the deposition of $Hg^{\cdot}$ ions present in small concentration in the solution,[1] upon the surface. The magnitude of the surface tension corresponding to this charging of the surface determines a definite position of the Hg in the S-shaped capillary K, which joins the two wide limbs A and B. When a negative current is sent through the capillary electrometer from the Hg meniscus in the capillary through the sulphuric acid to the Hg in the limb B, only the $Hg^{\cdot}$ ion concentration in the capillary and on the small meniscus surface is strongly altered (the latter is "polarised"), $Hg^{\cdot}$ ions adsorbed on the surface being discharged. This decrease of the positive charge corresponds to an increase

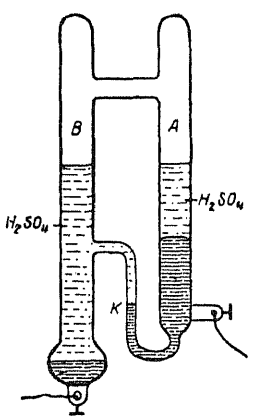

FIG. 61.

[1] Through solution of the oxide. Cf. footnote 1 on p. 197.

of the surface tension [1] and equilibrium is reached with a lower position of the Hg meniscus; in this case the meniscus falls when the circuit is made.

When the direction of the current is reversed the meniscus is positively polarised, so that the quantity of $Hg^{\cdot}$ ions on the meniscus surface and in the solution above it is increased; the electrical charge is increased and the surface tension decreases. Equilibrium is now reached at a higher position of the meniscus. In this case, therefore, on making the circuit the mercury rises in the capillary. If no current flows through the capillary electrometer, the position of the meniscus remains unaltered. This can be ascertained very precisely by illuminating the meniscus from behind with a small 2-volt lamp and a frosted plate, and looking at it with a microscope magnifying three to five times. If a setting is made so that the meniscus stands exactly on one of the divisions in the micrometer eye-piece, very small changes of its position can be seen without difficulty.

A capillary electrometer is filled as follows: the newly-made instrument, in which the two limbs A and B are open at the top is thoroughly cleaned by sucking through hot concentrated nitric acid, and washing out several times with distilled water. Pure distilled mercury is introduced into the limb A by means of a capillary pipette, until the meniscus stands about two-thirds of the way up the capillary K. It has been found that the best diameter for this capillary is $\frac{1}{2}$ to $\frac{3}{4}$ mm. The bulb of the other limb (B) is half-filled with mercury, and into both limbs a layer of pure, boiled-out 2N sulphuric acid is put so that the level in both limbs is below the cross connecting tube. One limb is now closed by fusion, and then, whilst evacuating, the other. If, in the course of use, the Hg meniscus becomes contaminated

[1] The effect may be looked upon as follows: the positively charged $Hg^{\cdot}$ ions situated on the mercury surface mutually repel and thereby keep the surface stretched. (This applies not only to the surface of the two menisci, in the capillary and the limb A, but to the whole surface where the mercury is against the glass walls, since the whole of the inner glass surface, which is not wetted by mercury, is covered by a thin layer of dilute sulphuric acid.) This force opposes the surface tension of the uncharged mercury, which tends to draw the surface together. Diminishing the number of $Hg^{\cdot}$ ions strengthens the influence of surface tension, while increasing the number weakens the effect. The fall and rise of mercury in the capillary is intelligible through the consideration that a decrease in surface corresponds to the strengthened effect of surface tension, the decrease in surface being effected by the passage of mercury out of the narrow capillary tube into the wide limb A; thus if a certain quantity of liquid is forced out of a narrow into a wide tube (without the narrow tube being emptied completely) the surfaces of this liquid depend upon the lengths of the corresponding columns, and these are inversely proportional to the cross-sections of the tubes, i.e. to the squares of the radii of the tubes.

(through anodic polarisation) or if small gas bubbles form (through cathodic polarisation) then by inclining the instrument some mercury can be poured off and the Hg surface in the capillary renewed.

(γ) *Electrometer Tapping Key.*—In order that the polarisation of the Hg meniscus in the capillary through the formation and removal of $Hg^{\cdot}$ ions when the current is passed through shall be rapidly removed, the capillary electrometer is always

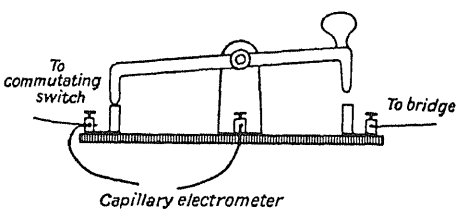

FIG. 62.—Electrometer key.

short-circuited after use, so that any concentration differences over the Hg in the limb B and over the meniscus in the capillary disappear (cf. concentration cells, p. 193). For this purpose the electrometer key shown in Fig. 62 is used for connecting in the capillary electrometer; when depressed, the current is allowed to pass through the instrument, while in the ordinary position the electrometer is short circuited.

(δ) *Commutating Switch.*—To facilitate connecting the normal

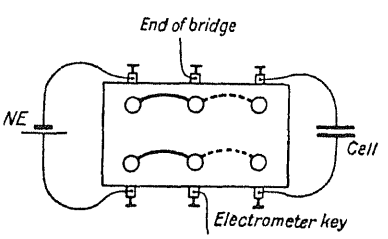

FIG. 63.—Commutating switch.

cell and the galvanic cell to be investigated quickly one after the other in the subsidiary circuit *b*KN*c* (Fig. 59) a commutating switch is used. It contains six Hg-filled cups, connected as shown in Fig. 63 with the electrometer key and the two cells. Changing over from the normal cell to the cell to be measured is done by moving across the wire hoops. If the E.M.F. of the unknown cell K is very small, it is connected in series with and in opposition to the normal element, as shown in Figs. 64 A and B.

The object of this is to bring the balance point near to the middle of the bridge wire, for the sake of the greater accuracy to be obtained there (cf. p. 3). If the E.M.F. measured is increased when the cell is connected in with the normal element, the two are in series (Fig. 64A; — pole of the N.E. connected to the + pole of the cell); if it is decreased, they are in opposition (Fig. 64B; — pole of the N.E. with the — pole of the cell). In this way the + and — poles of the galvanic cell can be determined.

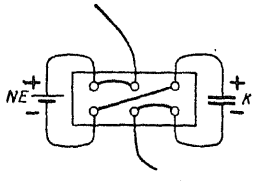

FIG. 64A.

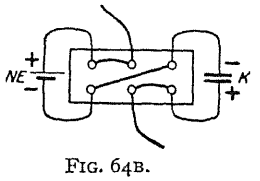

FIG. 64B.

(3) General Instructions for the Measurement of Electromotive Forces

(α) The accumulator is always connected up for a few minutes before beginning the measurement, since the E.M.F. always falls somewhat for a short time after it is connected.

(β) The balance position should be as near as possible to the middle of the bridge wire. If necessary the normal element is connected as described on page 188 to the cell to be measured.

(γ) Great care must be taken that the normal element is never connected in for more than a moment, particularly when still some way from the point of balance. It is necessary to be on guard against the risk of inadvertently short-circuiting it. A short-circuit alters the E.M.F. of the cell considerably, as a result of polarisation. The correct value is reached again only after a long period of rest (weeks or months).

(δ) Before and after every measurement of the unknown E.M.F. the accumulator must be standardised with the normal element. The settings of the normal element must agree to within 2 mm.; the average of the two settings is taken. For the causes of larger discrepancies, see page 184.

(ε) The accuracy of the measurement for cells with well-defined electrodes is about 2 to 3 millivolts (= 1 to 1·5 mm. on the bridge wire). With oxygen gas cells and oxidation cells with chromic acid it is considerably less.

(ζ) A cell is never measured immediately after being set up. A definite value is only reached after some time (*ca.* five to ten minutes).

(η) For each cell three independent settings are taken, all figures being recorded, as also for the repetitions of the normal element settings.

(θ) For every series of measurements a diagram is made in the notebook of the position of the commutating switch, the arrangement of the electrodes and the way in which they are connected to the commutating switch, somewhat as in the scheme in Figs. 65A and B.

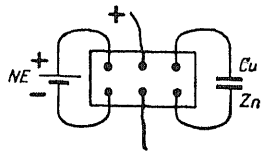

FIG. 65A.

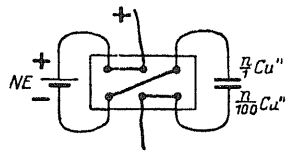

FIG. 65B.

(4) DIFFICULTIES AND SOURCES OF ERROR

(α) The capillary electrometer makes no response when connected either to the cell to be measured or to the normal element.

The apparatus is looked over from the point of view of the following questions:

Are all the terminals firmly screwed down?

Does the mercury in all the cups of the commutating switch reach the inner contacts which connect with the terminals outside?

Is a wire broken? Feel the wires, especially at any sharp bends.

Is the capillary electrometer properly connected up? Check over the connexions of the key by means of Fig. 62.

Is there a gas bubble in the capillary of the electrometer above the Hg meniscus? Pour out some mercury.

Is the Hg thread in the capillary separated from the Hg in the limb A by a layer of sulphuric acid? Pour some mercury out.

Is the electrometer capillary blocked by a white deposit? (This consists of Hg_2SO_4, formed by strong anodic polarisation of the Hg meniscus.) Pour some mercury out.

Is there contact between the sliding contact and the bridge wire? Clean the bridge wire from any oxide by rubbing with filter paper, *not* by scraping or scratching it with the knife edge of the sliding contact.

(β) The capillary electrometer responds only when one of the two cells (normal element or the cell to be measured) is connected in. There must be a break in the circuit in the cell for which there is no response. This is sought for as follows:

Do the wires in the small side tubes of the normal cell dip into the Hg?

Is there an air bubble in the bent tube of the half-element? (Fig. 66, p. 193.) It is removed by pressing the rubber tube between the screw clip and the apparatus. If necessary a fresh portion must be sucked up. Is the circuit broken in either of the electrodes?

To test this, they are individually bridged over, by pressing a bare Cu wire firmly against the terminal on top of the electrode, and dipping the end into the liquid between the electrodes. If the electrometer now responds, the break is in the electrode in question, which is removed and examined in detail. Either the lead wire is broken, or, with calomel electrodes, there is too much calomel on the mercury, so that the projecting point of the carbon electrode (Fig. 67, p. 195) is completely covered by calomel; or with gas electrodes (p. 204) the connecting wire fails to dip into the Hg through which contact is made with the platinum foil.

(γ) The capillary electrometer shows a deflection for all positions of the sliding contact. The following points should be examined:

Is it wrongly connected? (positive pole of the cell against the negative pole of the accumulator).

Is the accumulator really connected?

Has the particular circuit used (the cell in series with or in opposition to the normal element) happened to result in an E.M.F. approximately = 0 or 2 volts? A rough calculation should be made.

(δ) The position of balance changes with time, in the direction of an increasing value. In this case either a freshly charged accumulator has been used after too short a time (wait ten minutes) or the accumulator is too far discharged. In the first case the balance point will lie at about 50, and in the other case at about 56 cm.

(ϵ) The thread in the capillary electrometer "creeps."

In this case the capillary may be too narrow; such an instrument is usually of no use. Sometimes it can be used by not closing the circuit through it too frequently, and always waiting

as long as is required for the meniscus to return to its original position. Or the capillary may be contaminated by a deposit of Hg_2SO_4, in which case some mercury should be poured out. Or again, there may be a very high resistance in the subsidiary circuit *b*KN*c*. This is examined as under (β).

(ξ) The capillary electrometer shows a deflection although the key is not depressed. This happens when a non-insulated part of the electrometer key or of the leads to the electrometer is touched with the hand, and simultaneously the bridge wire is touched at some place other than the balance point, or any one of the terminals, or a bare wire on the commutator, or the electrodes is touched.

(η) Incorrect E.M.F. values are obtained when the Hg of the calomel electrode has been contaminated by zinc being dipped into it, or when a freshly prepared KCl or HCl solution is still unsaturated with Hg_2Cl_2; before use, these solutions must be shaken for at least two hours with excess of Hg_2Cl_2 on the automatic shaking machine.

B. PARTICULAR EXAMPLES OF CELLS

(1) Cells with Electrodes of the First Kind

The following cells will be studied experimentally:

(1) $Cu \Big/ \frac{M}{1} CuSO_4 \Big/ \frac{M}{1} ZnSO_4 \Big/ Zn.$

(2) $Cu \Big/ \frac{M}{100} CuSO_4 \Big/ \frac{M}{1} ZnSO_4 \Big/ Zn.$

(3) $Cu \Big/ \frac{M}{1} CuSO_4 \Big/ \frac{M}{100} CuSO_4 \Big/ Cu.$

(a) Theory

Since at the junction between the $CuSO_4$ and the $ZnSO_4$ solution there is no liquid potenti alto consider (because of approximate equality between the migration velocities of $Cu^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, and SO_4'', cf. p. 198), the total E.M.F. of each of these cells is equal to the difference between the single potentials of the electrodes (as discussed in the introduction, p. 179).

E for these cells is therefore :

(1) $\epsilon_{h\,Cu} - \epsilon_{h\,Zn}$.

(2) $\epsilon_{h\,Cu} + \frac{0{\cdot}058}{2} \log_{10} \frac{1}{100} - \epsilon_{h\,Zn}$.

(3) $\epsilon_{h\,Cu} - \left(\epsilon_{h\,Cu} + \frac{0{\cdot}058}{2} \log_{10} \frac{1}{100}\right) = -\frac{0{\cdot}058}{2} \log_{10} \frac{1}{100}$

$$= +\frac{0{\cdot}058}{2} \log_{10} \frac{100}{1}.$$

The cell (3) is a pure *concentration* cell. Both electrodes are of the same metal, but they are immersed in solutions of different concentrations. The two normal potentials therefore cancel out in the equation for E, leaving only a term depending upon the ratio of the concentrations of the solutions. For this reason it is said that the electrical energy of such a concentration cell is due to a purely osmotic process, namely the equalisation of concentration between the solutions.

(b) Experimental

The cells are built up of half-elements of the form shown in Fig. 66. The Zn electrode consists of a 1 cm. long, 4 mm. thick cylindrical Zn rod, to which a Cu wire lead is soldered. The Zn rod is sealed with picein wax so as to be watertight, into the lower end of a glass tube of suitable thickness, through which the Cu wire passes. Immediately before use the electrode is freshly amalgamated, which is done by dipping it for a short time into a solution of $HgNO_3$ which contains a drop of liquid mercury (to prevent oxidation). The more active Zn precipitates Hg upon its surface. After taking it out of the amalgamating liquid the Hg is rubbed with filter paper to obtain a uniform layer of amalgam. (The potential of the Zn is not altered by the amalgamation, since the amalgam saturated with Zn on its surface is in equilibrium with the massive Zn underneath, and when two metals are present simultaneously

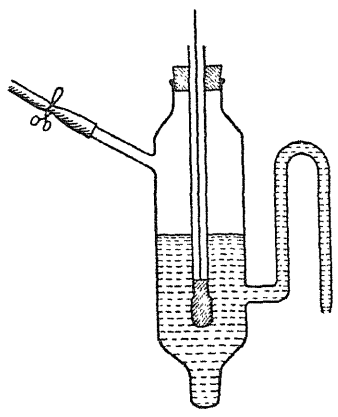

FIG. 66.—Half-element.

the potential is determined by the more active of the two.) The Cu electrode consists of a Cu rod similarly sealed with picein wax into a glass tube. Before the experiment it is freshly plated with Cu in a $CuSO_4$ solution, with an accumulator as source of current, for a few minutes. The other Cu electrode serves as anode, for this purpose.

The half-element is filled as follows: the vessel is closed with an airtight rubber stopper, through which the electrode passes; a short piece of rubber tubing with a spring clip is joined to the side tube. The bent tube is dipped into a beaker containing the solution, which is drawn in by suction applied to the rubber tube, until the half-element is about three-quarters full; the rubber tube is then closed with the clip. The two half-elements of the cell are held in a small stand at about the same height, and the two bent tubes are dipped into the intermediate liquid, contained in a crystallising dish or a small beaker. With cells 1 and 2 the intermediate liquid is 1M $ZnSO_4$, and with 3, 1M $CuSO_4$. The rubber stopper and the rubber tube must be quite airtight, so that no liquid flows out of the bent tube. The bent tube must be filled completely with liquid, and contain no air bubbles.

The E.M.F. of cell 3 is so small that the normal element must be connected in as well.

(2) Single Potentials

(a) Theory

The conception of "single" potentials has been discussed in the introduction. Instead of the normal hydrogen electrode the normal calomel electrode (mercury, covered with solid calomel, in contact with a 1N KCl solution saturated with calomel) is often used in the laboratory as a reference electrode, as it is very convenient in use, easily prepared, and its potential is accurately reproducible. Its potential with respect to the normal hydrogen electrode is + 0·283 volt at 18°. For the mechanism of the potential production, see page 197.

Just as in the use of the hydrogen electrode, the potential of the electrode being measured is given the + sign if it is positive in the combination with the calomel electrode, and the — sign if it is negative in the combination. The potential of the electrode in question against the normal hydrogen electrode is easily calculated from the potential measured against the calomel electrode, by adding to the latter (paying attention to

the sign) + 0·283. If the E.M.F. measured against the calomel electrode is negative and smaller (absolutely) than 0·283 volt, the sign becomes changed :

$$-0{\cdot}150 + 0{\cdot}283 = +0{\cdot}133 \text{ volt.}$$

(b) Experimental

(1) Preparation of the normal calomel electrode. Mercury which is pure for E.M.F. purposes (i.e. free from more active metals) is poured into the lower, narrow part of a half-element vessel to a depth of about $\frac{3}{4}$ cm., and covered with a thin layer of powdered calomel (at most 1 mm. deep) ; a carbon electrode (cf. 2) is dipped into the mercury to lead the current in, in such a way that the carbon point projecting from the glass tube is entirely under the surface of the mercury, and the rubber stopper in which the glass tube is held, closes the vessel to the air, at the top. The half-element is then filled, by suction, with a $\frac{N}{1}$ KCl solution which has been saturated with calomel by being shaken with excess of the salt for at least two hours on the automatic shaking machine. The bent tube of the calomel electrode always dips into a glass beaker containing $\frac{N}{1}$ KCl solution saturated in this way ; this applies when the electrode is not being used as well. When a measurement is being made against another electrode, this same KCl solution is always used as the intermediate liquid.

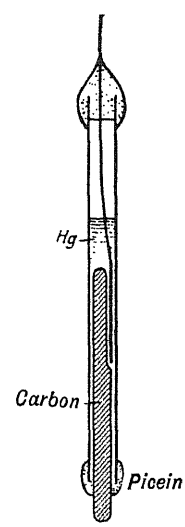

FIG. 67.—Carbon electrode.

(2) The preparation of the carbon electrode according to K. F. Herzfeld's directions is as follows : in a cylindrical carbon rod, *ca.* 4 cm. long and 4 mm. wide (the end of an arc lamp carbon rod) a groove is filed for a distance of about 2 cm. from one end, 1 mm. wide and 1 mm. deep. The rod is put into the lower end of a glass tube of suitable diameter and about 10 cm. length, so that the unfiled end protrudes about 1 cm., and is sealed in this position with picein wax, so as to be watertight. A bare copper wire with its end amalgamated is introduced from the open end of the glass tube, so that the amalgamated end lies in the filed groove, making as good contact as possible. (The

wire must be of sufficient strength.) The length of the wire is such that its upper end projects about 3 cm. out of the upper end of the glass tube. To improve the contact between the copper wire and the carbon some mercury is put in, and the upper end is then sealed with picein or sealing wax. (The usual platinum electrode with a platinum wire sealed into a mercury-filled glass tube is easily broken by careless handling at the seal, but the carbon electrodes are very robust. They can also be used in place of platinum electrodes for most oxidation and reduction cells.)

(3) Measurements are made with the following combinations :

$$Zn \Big/ \frac{M}{1}\ ZnSO_4 \Big/ \frac{N}{1}\ KCl \Big/ \text{Normal calomel electrode.}$$

$$Cu \Big/ \frac{M}{1}\ CuSO_4 \Big/ \frac{N}{1}\ KCl \Big/ \text{Normal calomel electrode.}$$

$$Cu \Big/ 0{\cdot}01\ M\ CuSO_4 \Big/ \frac{N}{1}\ KCl \Big/ \text{Normal calomel electrode.}$$

The single potentials of Cu in the two $CuSO_4$ solutions against the calomel electrode are so small that the normal element should be connected in.

From the potentials measured against the calomel electrode the potential differences with respect to the hydrogen electrode are calculated. The difference between two such potentials must agree with the directly measured E.M.F. of the corresponding cell.

(3) Cells with Electrodes of the Second Kind. Liquid Junction Potentials

The following cells are investigated :

1. $Hg \Big/ Hg_2Cl_2 \Big/ \frac{N}{1}\ KCl$, sat. with $Hg_2Cl_2 \Big/ \frac{N}{10}\ KCl$, sat. with $Hg_2Cl_2 \Big/ Hg_2Cl_2 \Big/ Hg$.
2. $Hg \Big/ Hg_2Cl_2 \Big/ \frac{N}{1}\ KCl$, sat. with $Hg_2Cl_2 \Big/ \frac{N}{100}\ KCl$, sat. with $Hg_2Cl_2 \Big/ Hg_2Cl_2 \Big/ Hg$.
3. $Hg \Big/ Hg_2Cl_2 \Big/ \frac{N}{10}\ KCl$, sat. with $Hg_2Cl_2 \Big/ \frac{N}{100}\ KCl$, sat. with $Hg_2Cl_2 \Big/ Hg_2Cl_2 \Big/ Hg$.
4. Similar to 1, but with HCl instead of KCl.
5. Similar to 2, but with HCl instead of KCl.
6. Similar to 3, but with HCl instead of KCl.
7. $Hg \Big/ Hg_2Cl_2 \Big/ 10$ c.c. $\frac{N}{1}\ HCl + 90$ c.c. sat. Na_2SO_4 soln. sat. with $Hg_2Cl_2 \Big/$ 10 c.c. $\frac{N}{10}\ HCl + 90$ c.c. sat. Na_2SO_4 soln. sat. with $Hg_2Cl_2 \Big/ Hg$.

The intermediate liquid is in every case the more concentrated solution.

(a) Theory

(1) The concentration cells studied now differ from the $Cu^{\cdot\cdot}$ concentration cells previously measured, in that here *electrodes of the second kind* are used. The essential feature of these is that a metal dips into the saturated solution of one of its salts, in the presence of the solid salt. The solution must also contain a salt with the same anion as the solid phase. Such electrodes are reversible both with respect to the cation and the anion.

The normal calomel electrode described above is an electrode of the second kind: it consists of Hg, covered with solid calomel, in a KCl solution saturated with Hg_2Cl_2. The seven cells now to be measured involve electrodes formed in the same way, differing only in the nature and concentration of the solution saturated with calomel. *The electromotively active metal is in every case mercury.* The E.M.F. of the different elements is therefore controlled only by the ratio of the $Hg^{\cdot}$ concentrations [1] in the two half-elements. Since at constant temperature in the presence of solid calomel the product $[Hg^{\cdot}] \times [Cl']$ must be constant (solubility product), it follows that a ten-fold increase in the Cl' concentration corresponds to a ten-fold-decrease in the $Hg^{\cdot}$ concentration.[2] The more concentrated Cl' solution is therefore the more dilute in $Hg^{\cdot}$ ions. Hence the cathode (+ pole) is the Hg in the more dilute KCl or HCl solution.

The reason for the reversibility of these electrodes of the second kind with respect to the anion is that with anodic solution of Hg to $Hg^{\cdot}$ the solubility product of calomel is exceeded, and precipitation of solid calomel causes a disappearance of Cl', while the cathodic discharge of $Hg^{\cdot}$ requires, for the re-establishment of the solubility product, solution of solid calomel, whereby the Cl' concentration is increased.

[1] Actually, the ions present in mercurous salts are mainly $Hg_2^{\cdot\cdot}$ ions; but since these are in equilibrium with $Hg^{\cdot}$ ions ($2Hg^{\cdot} \rightleftharpoons Hg_2^{\cdot\cdot}$), the quantitative statement of the relationships in terms of $Hg^{\cdot}$ ions is correct, and this will be done for the sake of greater simplicity in the formulæ.

[2] According to more recent views, it is only the *product of the activities* of the individual ions which is constant. The activities are obtained by multiplying the concentrations by the corresponding activity coefficients. For very dilute solutions the activity coefficients are = 1, so that here the solubility product and the product of the activities have the same value. This, however, is not the case when neutral *salts* are present in considerable concentration; the activity coefficients of the ions are influenced by their presence. The solubility product $[Hg^{\cdot}] \times [Cl']$ has not exactly the same value in the presence of $\frac{N}{1}$ KCl or HCl as in the presence of $\frac{N}{10}$ KCl or HCl. The differences are small enough for the considerations given above to be qualitatively valid, and approximately quantitatively.

(2) With respect to their *electrode potentials* the cell containing KCl and those containing HCl behave exactly alike. But they differ in that in the cells made up with HCl *diffusion-* or *liquid function potentials* come into play. These occur at the junction between solutions of different compositions, or of the same com position but of different concentrations; it is always a condition that ions of different migration velocities shall be present. In the present case, at the boundary $\frac{N}{1}$ HCl $\Big/ \frac{N}{10}$ HCl $H^{\cdot}$ ions and Cl' ions diffuse from the more concentrated solution into the more dilute, as a result of osmotic pressure differences. Because of their greater migration velocity (cf. table on p. 155) the $H^{\cdot}$ hurry ahead and charge the dilute solution positively with respect to the concentrated (Fig. 68). With KOH solutions the dilute solution would become negatively charged, since here the OH' migrates more quickly than the $K^{\cdot}$. In calculating the total potential difference of a cell from the two electrode

$$\frac{N}{1}\text{HCl}\ \begin{array}{c|c} - & + \\ Cl' & H^{\cdot} \\ Cl' & H^{\cdot} \\ Cl' & H^{\cdot} \\ Cl' & H^{\cdot} \\ Cl' & H^{\cdot} \end{array}\ \frac{N}{10}\text{HCl}$$

FIG. 68.

potentials and the liquid potentials, it must be remembered that the latter may either increase or diminish the value obtained for the difference of the electrode potentials. With a pure concentration cell the difference of the electrode potentials $\left(E = \frac{RT}{\nu \cdot F} \log_e \frac{c_1}{c_2}\right)$ is always greater than the liquid potential, as appears very clearly from formula 79; consequently the question which electrode is the cathode and which the anode can be decided without reference to the liquid potential, merely from the signs and values of the electrode potentials. Whether the liquid potential increases or decreases the potential difference calculated for the electrodes is decided as follows: if the solution in which the positive electrode dips, is itself charged positively by the liquid potential, then the positive charge of the electrode is strengthened; the liquid potential must therefore be added in order to obtain the total potential difference of the cell. If, on the other hand, this solution is negatively charged, the positive charge of the electrode is weakened; the liquid potential is then to be subtracted. In the case of calomel electrodes in hydrochloric acid the positive electrode is the one dipping in

the more dilute HCl, since there the concentration of $Hg^{\cdot}$ ions is greater, and so also their tendency to deposition. But this dilute solution is positively charged by the $H^{\cdot}$ migrating ahead; the liquid potential is therefore to be added in this case. If instead of calomel electrodes hydrogen electrodes were used, the electrode in the more concentrated HCl would be positive; in this case the liquid potential would have to be subtracted.

It is shown in theoretical text-books that the liquid potential between solutions of the same substance at different concentrations is given by the following formula:

$$E_l = \frac{u - v}{u + v} \cdot \frac{RT}{\nu F} \log_e \frac{c_1}{c_2} \quad . \quad . \quad . \quad (79)$$

With concentration cells containing KCl the liquid potential is negligible, since the mobility of $K^{\cdot}$ (equivalent conductance, $64{\cdot}4\ \Omega^{-1}$ cm.^{2}) is very nearly equal to that of Cl' ($65{\cdot}5\ \Omega^{-1}$ cm.^{2}). But with HCl the difference is very much greater: $H^{\cdot} = 315$, $Cl' = 65{\cdot}5$. The difference in E.M.F. of analogously constructed KCl and HCl concentration cells is determined simply by the liquid potential, and by subtracting the values of such analogous cells the liquid potential can be obtained directly from experimental data.

(3) Elimination of liquid junction potentials: their presence can be to a large extent avoided by two devices:

(α) Instead of allowing the two solutions to join directly, an intermediate liquid ("salt bridge") is inserted, consisting of a saturated KCl solution, for which the ions move at equal speeds. If this is not applicable, a concentrated KNO_3 or $(NH_4)NO_3$ solution can be used.

(β) The two liquids are allowed to come into direct contact, but to each a supplementary electrolyte is added at the same high concentration, which neither itself influences the electrode potentials nor forms a chemical compound with the ions which determine the electrode potentials. This procedure is applied with cell 7: the same quantity of saturated Na_2SO_4 solution is added to both electrode liquids. Clearly the effect of this addition will be to neutralise the charging-up of the double layer at the junction of the pure HCl solutions of different concentrations, through the presence of $Na^{\cdot}$ and SO_4'' ions in high concentration. Thus the diffusion potential is found as the difference of the E.M.F.'s of analogous HCl solutions with and without the addition of sodium sulphate.

(b) Experimental

The single electrodes are prepared exactly as described for the normal calomel electrode. The intermediate liquid is always the more concentrated of the two solutions. The total potential differences are so small that the measurement must be made with the normal element in series. The E.M.F.'s of the seven cells are to be recorded, together with the measured and calculated liquid potentials.

(4) Determination of the Solubility of a Very Slightly Soluble Salt by Means of the E.M.F. of a Concentration Cell

The cell to be measured is :

$$\text{Ag, solid AgCl} \Big/ \frac{N}{10}\,\text{KCl, sat. with AgCl} \Big/ \frac{N}{10}\,\underset{\text{Intermediate liquid.}}{\text{KNO}_3} \Big/ \frac{N}{10}\,\text{AgNO}_3 \Big/ \text{Ag.}$$

(a) Theory

(1) In this combination the positive electrode (cathode) is an electrode of the first kind, the negative electrode (anode) of the second kind. To the latter are applicable the considerations given above (p. 197) for the normal calomel electrode: because of the constancy of the solubility product of AgCl the concentration of $Ag^{\cdot}$ ions is here determined by the concentration of Cl' ions. The concentration of Cl' is known. That of the $Ag^{\cdot}$ is calculated as follows from the measured E.M.F. of the cell: If $c_{Ag^{\cdot}}$ is the $Ag^{\cdot}$ concentration in the $\frac{N}{10}$ $AgNO_3$ solution and $c'_{Ag^{\cdot}}$ the unknown $Ag^{\cdot}$ concentration in the $\frac{N}{10}$ KCl solution, then :

$$E = \frac{RT}{1F}\log_e \frac{c_{Ag^{\cdot}}}{c'_{Ag^{\cdot}}} = 0{\cdot}058 \log_{10} \frac{c_{Ag^{\cdot}}}{c'_{Ag^{\cdot}}} = 0{\cdot}058\,(\log_{10} c_{Ag^{\cdot}} - \log_{10} c'_{Ag^{\cdot}})\,;$$

$$\log_{10} c'_{Ag^{\cdot}} = \log_{10} c_{Ag^{\cdot}} - \frac{E}{0{\cdot}058} = \log_{10} \frac{K}{c_{Cl'}}\,,$$

where K is the solubility product of AgCl.

$c_{Ag^{\cdot}}$ is put $= 0{\cdot}082$, since the apparent degree of dissociation of a $\frac{N}{10}$. $AgNO_3$ solution is 0·82 ; $c_{Cl'}$ in a $\frac{N}{10}$ KCl solution is 0·085 mol/litre. Multiplication of the calculated $c'_{Ag^{\cdot}}$ by this Cl' concentration gives the solubility product K of AgCl at the temperature of the experiment. The same product is reached

when solid AgCl is in equilibrium with its saturated solution in pure water (cf. p. 209) at the same temperature. Assuming that the dissolved AgCl is practically completely dissociated, then $c_{Ag^{\cdot}} = c_{Cl'} = \sqrt{K}$. This concentration corresponds to the AgCl content of the saturated solution in water, and therefore gives the solubility of solid AgCl.

(2) The process which proceeds spontaneously in this cell and produces electrical work, is ascertained by a consideration of the changes taking place in the cathode and anode spaces during the passage of 1F. In the cathode space 1 mol of $Ag^{\cdot}$ of concentration $\frac{N}{10}$ disappears, by the ions depositing themselves as metal. In the KCl solution 1 mol of Ag metal dissolves anodically. The $Ag^{\cdot}$ ions formed immediately combine with 1 mol Cl' of concentration $\frac{N}{10}$ to form 1 mol of undissociated AgCl which precipitates out. In the electrolyte the current is carried from one solution to the other chiefly by the $K^{\cdot}$ and NO_3' ions.[1] Since the transport of silver metal from one electrode to the other does not involve any work, the only processes which have to be considered as producing work are the disappearance of 1 mol $Ag^{\cdot}$ and 1 mol Cl' of concentration $\frac{N}{10}$ and the formation of 1 mol of solid AgCl. With the ionic concentrations given this process takes place spontaneously, and since it is conducted reversibly, it can do work.

$$E \,.\, F = RT\,(\log_e c_{Ag^{\cdot}} - \log_e c'_{Ag^{\cdot}}) = RT\left(\log_e c_{Ag^{\cdot}} - \log_e \frac{K}{c_{Cl'}}\right)$$

$$= RT \log_e \frac{c_{Ag^{\cdot}} \,.\, c_{Cl'}}{K} = \frac{RT}{0{\cdot}4343} \,.\, \log_{10} \frac{c_{Ag^{\cdot}} \,.\, c_{Cl'}}{K} \qquad . \quad (80)$$

If the ions which are removed did not have these large concentrations, but instead had concentrations such that their product was equal to the solubility product K, then in equation (80) the numerator of the fraction under the log sign would be equal to the denominator; but $\log_{10} 1 = 0$, i.e. in this case no work could be done and no current produced, because no spontaneous AgCl formation would occur.

[1] During the passage of 1F there is also a transfer of *ca.* $\frac{1}{2}$ equivalent of NO_3' ions from the $AgNO_3$ solution into the KCl solution, and of *ca.* $\frac{1}{2}$ equivalent of $K^{\cdot}$ ions in the reverse direction. Since, however, there is no force opposing these processes, they take place irreversibly and consequently without actual production of work.

(b) Experimental

For the silver electrodes pieces of silver wire are used, 4 cm. long and 1 mm. thick; these are welded in a non-luminous Bunsen flame to the ends of 10 cm. long copper wires, and sealed with picein wax into 8 cm. glass tubes, so that about 3·5 cm. of the silver wire protrudes. This end is twisted in a spiral form round the end of the glass tube (cf. Fig. 53, p. 171). By means of rubber stoppers the electrodes are fastened into the half-elements so as to be airtight. Immediately before the experiment the two electrodes are silver-plated for one minute each in the silvering solution (cf. p. 172) with an accumulator as source of current, and a small silver wire as anode. They are then washed and dried by shaking them in the air—not in the oven, since the picein wax melts. On dipping the two silver electrodes simultaneously into $\frac{N}{10}$ $AgNO_3$ solution they should show no potential difference. This is tested in the compensating circuit, by connecting the cell in series with the normal element (cf. p. 188); the setting of the normal element should not be altered. If there is a detectable potential difference, it can be removed by short-circuiting the two electrodes for some time in the $AgNO_3$ solution.

The saturation of the $\frac{N}{10}$ KCl solution with AgCl is produced by means of a drop of $AgNO_3$ solution, which must produce a permanent precipitate.

Record the E.M.F. of the cell; the concentration of $Ag^{\cdot}$ ion in the KCl solution; the solubility product and the solubility of AgCl.

(5) Gas Cells

Two elements are measured:

(1) Pt sat. with H_2 at 1 atm. / $\frac{N}{1}$ HCl / $\frac{N}{1}$ KCl / normal calomel electrode.

(2) Pt sat. with H_2 at 1 atm. / $\frac{N}{1}$ KOH / $\frac{N}{1}$ KCl / normal calomel electrode.

The two E.M.F.'s are corrected for the liquid potentials; from this the difference of the electrode potentials is calculated for the cell:

(3) Pt sat. with H_2 at 1 atm. / $\frac{N}{1}$ HCl / $\frac{N}{1}$ KCl / $\frac{N}{1}$ KOH / Pt sat. with H_2 at 1 atm.

The value of this could be measured directly by constructing cell 3 in such a way as to avoid the liquid potential (cf. p. 199).

(a) Theory

If a platinum plate is saturated with hydrogen gas, the gas in metallic solution behaves electromotively just as though it were a massive metal: when dipped into a solution of $H^{\cdot}$ ions it possesses a definite solution pressure, which depends upon the gas pressure over the electrode during the measurement. From two platinum plates saturated with H_2 at atmospheric pressure, and two solutions of different $H^{\cdot}$ concentration a concentration cell can be made, exactly as with two Cu electrodes in $Cu^{\cdot\cdot}$ solutions of different concentrations (cf. p. 192, cell 3). Just as it is possible with such a $Cu^{\cdot\cdot}$ concentration cell to calculate the potential difference of the complete cell from the single potentials of the two electrodes against the normal calomel electrode (cf. p. 196), so the E.M.F. of the gas cell may be obtained from the single potentials measured by means of the combinations 1 and 2. It must be taken into account, however, that single potentials as directly measured contain also the liquid potentials which exist at the junctions $\frac{N}{1}$ HCl $\Big/ \frac{N}{1}$ KCl and $\frac{N}{1}$ KOH $\Big/ \frac{N}{1}$ KCl. In this case, where solutions of the same concentration of different electrolytes come into contact, the calculation of the liquid potential is made by means of the formula:

$$E_l = \frac{RT}{\nu F} \log_e \frac{u_1 + v_2}{u_2 + v_1} \quad . \quad . \quad . \quad (81)$$

u and v are the migration velocities of the ions (cf. the table on p. 155). Ions of the same solution are denoted by the same subscript. The easiest way to avoid errors of sign is to allot the subscripts in such a way that $u_1 + v_2$ is greater than $u_2 + v_1$, so that the calculated value of E_l is positive in any case. Whether this amount is to be added or subtracted from the measured E.M.F. of the cell in order to obtain the potential due to the electrodes alone, is decided on the basis of a qualitative consideration, referring to the remarks on page 198. In cell 1, where HCl and KCl come into contact, the anions are the same in the two solutions, so that the liquid potential is governed by the difference between the migration velocities of the cations; the $H^{\cdot}$ migrate more quickly than the $K^{\cdot}$, so that the KCl solution becomes positively charged. In cell 2, where the junction is between KOH and KCl, the cations are the same and the difference between the migration velocities of the anions produces the liquid potential. The quicker OH' charges the KCl solution negatively.

Subtraction of the two single potentials (corrected in this way) gives the E.M.F. of cell 3 with the liquid potentials eliminated, which would arise at the junctions HCl/KCl and KCl/KOH, if the cell were actually constructed. From this E.M.F. a calculation can be made (analogous to the calculation for AgCl, p. 200) with the aid of the known $H^{\bullet}$ concentration of the $\frac{N}{1}$ HCl, of the unknown $H^{\bullet}$ concentration in the $\frac{N}{1}$KOH, and hence the value of the ionic product $[H^{\bullet}] \times [OH']$. The apparent concentration of $H^{\bullet}$ in $\frac{N}{1}$HCl, and of OH' in $\frac{N}{1}$KOH, is 0·8 mol/litre. The process producing work is the formation of H_2O from $H^{\bullet}$ and OH' of the given concentrations, so that the free energy of the neutralisation process in such solutions is obtained in this way.

The unknown $H^{\bullet}$ concentration in other solutions can be determined as in the 1N KOH solution, by immersing a hydrogen gas electrode and measuring the potential against a normal hydrogen electrode, or more simply, against a normal calomel electrode. The method is of great importance for physiological investigations. The liquid potentials which occur must either be corrected for, or their occurrence avoided by the use of the devices described on p. 199. Cf. also the quinhydrone electrode, p. 211.

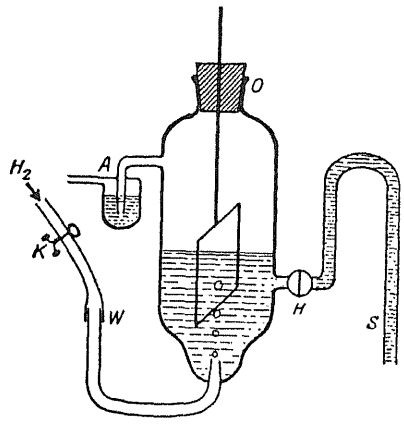

FIG. 69.—Gas electrode.

(b) Experimental

The gas electrode has the form shown in Fig. 69. It is constructed in the following manner: the platinum electrode is cautiously removed from the thick-walled test-tube which protects it, washed several times with distilled water and dried by dipping in absolute alcohol and shaking in the air. Whilst doing so it is necessary to avoid touching the electrode surface, which is covered all over with platinum black, with the fingers, or breaking it off at the seal. If the coating is defective and the

bare metal showing through, it must be re-platinised. (For instructions for platinising, see p. 163). The introduction of the current is most simply done by means of a mercury-filled glass tube, through the lower end of which is sealed a platinum wire (welded to the electrode surface), and into which a copper passes from the top. (Not shown in the simplified diagram of Fig. 69.) The electrode is fastened (airtight) by means of the rubber stopper, in the opening O; the rubber tube serving as the in-lead for the H_2 is joined on at W and closed by the screw-clip K immediately above W. The bent glass tube S in a beaker containing $\frac{N}{1}$ HCl or $\frac{N}{1}$ KOH, and by suction at A, after opening the tap H, liquid is drawn in until the platinum plate is half immersed. The H is closed, K opened and the stream of hydrogen started. The hydrogen is prepared in a Kipp's apparatus from Zn and HCl, washed in two wash bottles with potassium permanganate and alkaline pyrogallol, and is bubbled through the electrode at such a rate that the bubbles can be counted easily. A little water is introduced into A with a pipette, as a seal against the air outside. There must be no gas bubble in the syphon tube HS. The end S dips into $\frac{N}{1}$ KCl as the intermediate liquid. The tap H should not be greased; if it is wetted all round by turning it round several times, the liquid in the barrel of the tap conducts well enough for measurements to be made with the tap closed. In this way diffusion of the intermediate liquid into the electrode vessel is prevented. The measurement is begun after bubbling the gas through for half an hour. It is repeated at intervals of quarter of an hour until the potential has become constant to within 2 millivolts. After measuring cell 1 with HCl the platinum electrode and the electrode vessel are thoroughly washed with distilled water and dried, and then filled with KOH.

Record the single potentials measured; the calculated liquid potentials; the single potentials corrected for the liquid potentials; the difference of the corrected potentials; the $H^{\cdot}$ concentration in $\frac{N}{1}$ KOH; the ionic product of water.

(6) Oxidation-reduction Cells

(a) Theory

(1) In the cells considered so far, the process governing the potential consisted of the passage of elements into the ionic

state by taking up electrons, or of ions into the state of the neutral element by giving up electrons. Definite potentials can also be obtained by immersing a permanent electrode in a solution containing a mixture of substances capable of changing into one another by taking up or giving up electrons, so that the oxidation and reduction process (which with a non-permanent electrode ($Cu \rightleftharpoons Cu^{\cdot\cdot}$) occurs at the electrode) here takes place in the solution itself, e.g. $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$; $Sn^{\cdot\cdot} \rightleftharpoons Sn^{\cdot\cdot\cdot\cdot}$; hydroquinone $\rightleftharpoons$ quinone (in the quinhydrone electrode).

Two such processes can be combined together to form a cell, e.g.:

$$\text{Pt} \left| \begin{matrix} Fe^{\cdot\cdot} \\ Fe^{\cdot\cdot\cdot} \end{matrix} \right| \begin{matrix} Sn^{\cdot\cdot} \\ Sn^{\cdot\cdot\cdot\cdot} \end{matrix} \left| \text{Pt.} \right.$$

So also the total E.M.F. of such an oxidation-reduction cell may be divided up into single potentials. The formula for the single potential measured against the normal hydrogen electrode is, for example,

$$E = \frac{RT}{\nu F} \log_e \frac{c_{0Fe^{\cdot\cdot}}}{c_{0Fe^{\cdot\cdot\cdot}}} + \frac{RT}{\nu F} \log_e \frac{c_{Fe^{\cdot\cdot\cdot}}}{c_{Fe^{\cdot\cdot}}} \quad . \quad . \quad (82)$$

When $c_{Fe^{\cdot\cdot}}$ and $c_{Fe^{\cdot\cdot\cdot}} = 1$, the second term vanishes, and the E.M.F. given by the first term corresponds to the process taking place in the cell at these concentrations:

$$Fe^{\cdot\cdot\cdot} + \tfrac{1}{2}H_2 = Fe^{\cdot\cdot} + H^{\cdot}.$$

This E.M.F. is again referred to as the normal potential, and gives the potential measured against the normal hydrogen electrode, to which the electrode becomes charged, when both kinds of ions are present in one molar concentration. If $\frac{c_{Fe^{\cdot\cdot}}}{c_{Fe^{\cdot\cdot\cdot}}} = \frac{c_{0Fe^{\cdot\cdot}}}{c_{0Fe^{\cdot\cdot\cdot}}}$, then against the normal electrode $E = 0$; no current flows, i.e. the state is one of equilibrium. A platinum electrode dipping in a solution with this ionic concentration ratio shows no potential difference with respect to the normal hydrogen electrode.

(2) The total potential may equally well be calculated by considering the *total process* taking place in the cell, and equating the maximum work which it can produce, to the electrical work. A determination of the E.M.F. of such a cell provides, therefore, a measure of the affinity with which this total process takes place.

The cell which will be investigated is

$$\text{Carbon} \left| \begin{matrix} Fe^{\cdot\cdot} \\ Fe^{\cdot\cdot\cdot} \end{matrix} \right| \frac{N}{10} KNO_3 \left| \begin{matrix} HCrO_4' \\ Cr^{\cdot\cdot\cdot} \\ H^{\cdot} \end{matrix} \right| \text{Carbon.}$$

At the concentration given below for the different solutions, the cell works in such a way that $HCrO_4'$ is reduced at one electrode and $Fe^{\cdot\cdot}$ is oxidised at the other. The total process is expressed by the equation

$$HCrO_4' + 3Fe^{\cdot\cdot} + 7H^{\cdot} = Cr^{\cdot\cdot\cdot} + 3Fe^{\cdot\cdot\cdot} + 4H_2O.$$

If the concentrations at which the various ions are present are expressed by square brackets, and equilibrium concentrations are indicated by the suffix $_0$, then by means of the van't Hoff reaction isotherm the maximum work of this process is calculated to be

$$\begin{aligned} A &= RT \log_e \frac{[Cr^{\cdot\cdot\cdot}]_0 [Fe^{\cdot\cdot\cdot}]_0^3}{[HCrO_4']_0 [Fe^{\cdot\cdot}]_0^3 [H^{\cdot}]_0^7} \\ &\quad + RT \log_e \frac{[HCrO_4'] [Fe^{\cdot\cdot}]^3 [H^{\cdot}]^7}{[Cr^{\cdot\cdot\cdot}] [Fe^{\cdot\cdot\cdot}]^3} \\ &= RT \log_e K + RT \log_e \frac{[HCrO_4'] [Fe^{\cdot\cdot}]^3 [H^{\cdot}]^7}{[Cr^{\cdot\cdot\cdot}] [Fe^{\cdot\cdot\cdot}]^3} \quad . \quad (83) \end{aligned}$$

Since the water is present in great excess, its concentration can be taken as constant; so that in the expression for the maximum work it cancels out.

If the affinity of this reaction is determined by measurement of the E.M.F. of the cell described above by the compensation method, the electrical work for the change according to the above equation is 3 . E . F, since the reduction taking place at the cathode according to the equation

$$HCrO_4' + 7H^{\cdot} + 3 \ominus = Cr^{\cdot\cdot\cdot} + 4H_2O,$$

and the oxidation at the anode according to the equation

$$3\ Fe^{\cdot\cdot} - 3 \ominus = 3\ Fe^{\cdot\cdot\cdot},$$

involve the transfer of 3F. The E.M.F. is therefore

$$E = \frac{RT}{3F} \log_e K + \frac{RT}{3F} \log_e \frac{[HCrO_4'] [Fe^{\cdot\cdot}]^3 [H^{\cdot}]^7}{[Cr^{\cdot\cdot\cdot}] [Fe^{\cdot\cdot\cdot}]^3} \quad . \quad (84)$$

(3) This expression shows how the E.M.F. of the cell is affected by additions made to the separate solutions. E rises with increase of $H^{\cdot}$ concentration, e.g. by addition of sulphuric acid to the chromate electrode, and falls when it is decreased, e.g. by addition of sodium acetate or sodium hydroxide. It also rises with decrease of $Fe^{\cdot\cdot\cdot}$ concentration, e.g. by addition of sodium acetate to the $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ electrode, whereby $Fe^{\cdot\cdot\cdot}$ is bound into a complex. Decrease of $Fe^{\cdot\cdot}$ concentration causes

a decrease in E, e.g. by addition of sodium oxalate, which binds $Fe^{\cdot\cdot}$ in a complex.

(b) Experimental

The solutions are prepared as follows: equal volumes of a 10 per cent ferrous sulphate solution ($FeSO_4 . 7H_2O$), or of a 14·1 per cent solution of Mohr's salt $(NH_4)_2 Fe(SO_4)_2 6H_2O$, and of a 5 per cent. solution of ferric alum $KFe(SO_4)_2 . 12H_2O$ are mixed and introduced into one half-element. In the other is a solution prepared by mixing 100 volumes 5 per cent. potassium chromate solution and 1 volume of 0·1 per cent. chromic alum $KCr(SO_4)_2 . 12H_2O$ solution. Carbon electrodes (as used for the calomel electrodes (p. 195) serve as electrodes. The intermediate liquid is $\frac{N}{10} KNO_3$. It is necessary to wait at least quarter of an hour after setting up the cell before beginning the measurement; perfect constancy is never obtained with cells containing chromic acid. Further measurements are then made on the two half-elements separately against the normal calomel electrode, investigating the influence of the following added substances:

(*a*) Additions to the $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ electrode:
1. Two to three drops of concentrated sulphuric acid.
2. Solid sodium acetate until a dark brown coloration is obtained.
3. Solid ammonium oxalate.

(*b*) Additions to the chromate electrode:
1. Two to three drops of concentrated sulphuric acid.
2. Five to ten drops of concentrated sulphuric acid.
3. Solid sodium acetate in excess.
4. Solid caustic soda, until the solution clears again and a strongly alkaline reaction is produced.

The additions should be made one after the other, in the sequence given, to the solutions in the half-elements.

Record: the E.M.F. of the complete cell; the single potentials against the calomel and the hydrogen electrodes; alteration in the single potentials by the addition of the substances mentioned.

(7) Potentiometric Titrations

(a) Theory

With all serviceable titration methods, very small additions of the measuring liquid in the neighbourhood of the equivalent point produce large *relative* changes in the concentration of the ions involved in the titration process. This is most easily seen by working through an example, such as the titration of 100 c.c. of a $\frac{N}{10}$ $AgNO_3$ solution with a $\frac{N}{10}$ KI solution. The solubility product of the silver iodide produced is *ca.* 10^{-16}. Since solid silver iodide is present throughout the titration, the product $[Ag^{\cdot}] \times [I']$ must always have approximately the same value.[1] Assuming complete dissociation the initial concentration of $Ag^{\cdot}$ ions is 10^{-1}. If the additions of KI are so chosen that the $Ag^{\cdot}$ concentration is altered by one power of 10 each time, then by the addition of about 82 c.c. of the KI solution it falls to 10^{-2}. (The quantity of $Ag^{\cdot}$ ions present in 18 c.c. of the original solution remains, and is now contained in 182 c.c. of total solution.) The decrease by another power of 10 to 10^{-3} is reached by the addition of about 16 c.c. more of the KI solution (2 c.c. $\frac{N}{10}$ $A^{\cdot}$ ion solution in 198 c.c. of total solution), while to reduce it to a concentration of 10^{-4} only 1·8 c.c. KI solution are required. If now a further 0·18 c.c. KI solution are added, the $Ag^{\cdot}$ concentration becomes $= 10^{-5}$ (in all $82 + 16 + 1{\cdot}8 + 0{\cdot}18 = 99{\cdot}98$ c.c. KI, and 0·02 c.c. $\frac{N}{10}$ $Ag^{\cdot}$ still unprecipitated, in 200 c.c.). With a further 0·02 c.c. the equivalent point ($Ag^{\cdot}$ ion concentration $= I'$ ion concentration $= 10^{-8}$) is reached. This last almost infinitesimal addition has therefore produced a concentration change of three powers of 10. If the addition of KI solution is continued beyond the equivalent point, the result is the "mirror-image" of the foregoing process: an excess of KI solution of 0·02 c.c. gives a I' ion concentration of 10^{-5} (0·02 c.c. $\frac{N}{10}$ KI

[1] In the course of a titration neutral salts are being produced continuously (in this case KNO_3) and their concentration changes as the titration proceeds. This alters the solubility and the solubility product (solubility $= \sqrt{\text{solubility product}}$; cf. p. 197). Thus with uni-univalent electrolytes the solubility in the presence of a 0·1N neutral salt solution which contains no common ion and forms no complex ion, the solubility is increased 10 per cent. and the solubility product therefore about 20 per cent. as compared with the value in pure water.

solution in *ca.* 200 c.c. of total solution), and therefore an $Ag^{\cdot}$ ion concentration of 10^{-11}. The next 0·2 c.c. raises the I′ ion concentration to 10^{-4} and decreases that of the $Ag^{\cdot}$ ion to 10^{-12}. The alteration of a further power of 10 requires 2 c.c. KI solution, and for the next power as much as 20 c.c. KI solution are necessary. If these facts are tabulated and represented graphically (Fig. 70) the following survey is obtained :—

100 c.c. $\frac{N}{10}$ $AgNO_3$	$Ag^{\cdot}$ ion concentration	10^{-1}
+ 82 c.c. $\frac{N}{10}$ KI	,, ,,	10^{-2}
+ 16 ,, ,,	,, ,,	10^{-3}
+ 1·8 ,, ,,	,, ,,	10^{-4}
+ 0·18 ,, ,,	,, ,,	10^{-5}
+ 0·02 ,, ,,	,, ,,	10^{-8}
+ 0·02 ,, ,,	,, ,,	10^{-11}
+ 0·2 ,, ,,	,, ,,	10^{-12}
+ 2 ,, ,,	,, ,,	10^{-13}
+ 20 ,, ,,	,, ,,	10^{-14}

If an electrode, the potential of which is determined by the concentration of the ions which are of importance, is dipped in

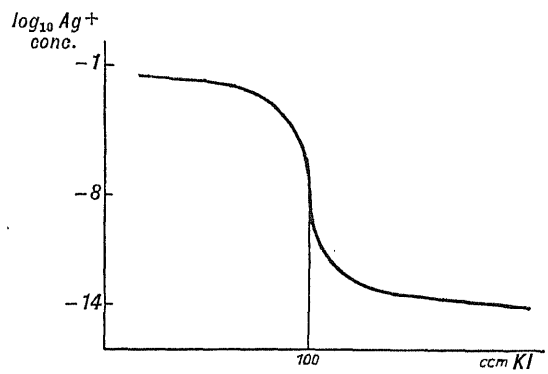

FIG. 70.—Titration curve.

the solution to be titrated, then in the case of univalent ions the potential changes by 0·058 volt (cf. p. 182) for every alteration in the concentration of one power of 10. By combining the electrode with an electrode of constant potential (e.g. a hydrogen or calomel electrode) into a galvanic cell, the course of the titration can be followed whilst the titrating liquid is being added by means of the E.M.F. of this cell. For example, in the case considered above, when the potential is plotted against the amount of KI solution added a curve is obtained of the same

form as Fig. 70 (or its mirror-image). The equivalent point appears as the point of inflexion of the curve.

The method is of service in the quantitative determination of many metals, and by using a hydrogen electrode, for acidimetry and alkalimetry, and for many oxidation and reduction titrations.

References :—
Kolthoff and Furman. Potentiometric Titrations, 1918.
H. S. Taylor. Chap. XII, pp. 842-54.

(b) Experimental

The content of an unknown KCl solution is determined potentiometrically. The following cell is made up :

$$Ag^{\cdot}\Big/\frac{N}{10}\,AgNO_3/\text{sat. }KNO_3\Big/\frac{N}{10}\,AgNO_3/Ag.$$

One of the half-elements is replaced by a beaker with 100 c.c. 0·1N $AgNO_3$, into which the KCl solution to be determined is run from a burette. After every addition the E.M.F. is measured in the compensation circuit. The connexion between the beaker and the intermediate liquid is effected by means of a U-shaped syphon provided with a glass tap in the bend. The syphon is filled with the saturated KNO_3 solution, by holding it with the open end upwards and the tap open. The ungreased tap is then closed, when the syphon can be inverted and set in the solutions without the contents running out.

Record : the normality of the KCl solution ; a graph of the titration : ordinates E.M.F. ; abscissæ : c.c. of KCl solution added.

(8) Measurement of Hydrogen Ion Concentration with the Quinhydrone Electrode

(a) Theory

Quinhydrone is an addition product of hydroquinone and quinone. A bare platinum or gold solution immersed in a saturated aqueous quinhydrone electrode behaves, in virtue of the oxidation-reduction potential of quinhydrone (quinone $\rightleftharpoons$ hydroquinone ; cf. p. 206), like a hydrogen electrode with a definite (and very low) gas pressure. As with the hydrogen electrode, the potential of the quinhydrone solution depends upon the concentration of $H^{\cdot}$ ions in the solution. This electrode however, only gives correct results in the acid or weakly alkaline region, and does not work in solutions of smaller $H^{\cdot}$ concentration

than 10^{-8}. Also the presence of electrolytes in concentration higher than 0·1 mol/litre causes erroneous results. The latter effect can be eliminated by saturating the solution to be investigated not only with quinhydrone but also with quinone or hydroquinone. For saturation it is necessary to shake the solution for several hours with both solid substances. The saturation of aqueous solutions with quinhydrone alone is most simply done by pouring a saturated alcoholic quinhydrone solution into the solution in question, whereby the quinhydrone, because of its smaller solubility in water, precipitates out.

(b) Experimental

The p_H of an acid solution is determined by the quinhydrone electrode. The following cell is constructed and its E.M.F. measured :

$$Pt\Big/\frac{N}{10}\ HCl \text{ sat. with quinhydrone/sat. KCl/normal calomel electrode.}$$

In a second experiment the unknown solution (saturated with quinhydrone) is substituted for the $\frac{N}{10}$ HCl. The saturation is obtained in each case by pouring in a saturated alcohol solution of quinhydrone. If saturated (3·5 molar) KCl solution is used as the intermediate liquid, the liquid potentials can be neglected. Dividing the difference of the E.M.F.s of the two cells by 0·058 volt gives the number of powers of 10 by which the $H^{\cdot}$ ion concentration differs from the $\frac{N}{10}$ HCl.

Record the measured E.M.F.s of the two cells ; the p_H and the $H^{\cdot}$ ion concentration (in mol/litre) of the unknown solution.

XVIII. ELECTROCHEMICAL PREPARATIONS

General Theory

(1) DURING the passage of the current in any electrolysis an E.M.F. is set up which opposes the potential applied externally; this is the "polarisation E.M.F." For the electrolysis to proceed continuously the applied potential must exceed the polarisation E.M.F. With a given electrolytic resistance W, the current strength I set up in accordance with Ohm's law is determined only by the amount by which the external potential exceeds the polarisation E.M.F.: external potential E_e = polarisation E.M.F. $E_p + I \cdot W$ (Ohm's law potential fall).

(2) The causes of the polarisation are the potential "steps" which are set up during the electrolysis at the contact between the electrodes and the electrolyte. They arise in the same way as in a galvanic cell, since as a result of the passage of the current in the electrolysis cell a concentration, gas, or oxidation-reduction cell is produced. For example, if a copper sulphate solution is electrolysed between copper electrodes, in the absence of very vigorous stirring, the concentration of $Cu^{\cdot\cdot}$ increases at the anode through solution of metallic copper, and decreases at the cathode through its precipitation. This sets up a *concentration cell*, the E.M.F. of which enters into the phenomenon of electrolysis as a polarisation E.M.F., the magnitude of which can be calculated from a knowledge of the concentration difference which exists, by means of the ordinary formula for concentration cells.

In almost all cases of electrolysis of dilute aqueous solutions between permanent electrodes oxygen is produced at the anode and hydrogen at the cathode, so that a *gas cell* is set up. As the gas pressure at the two electrodes rises the polarisation E.M.F. also increases up to a maximum, when the gas pressure on both sides reaches 1 atmosphere and the gases are evolved in the form of bubbles. Here the phenomenon of "over-voltage" appears under certain circumstances (see below).

Electrolysis between permanent electrodes can also result in

changing the ionic charge—*i.e.*, reduction at the cathode (= addition of electrons: $Cu^{\cdot\cdot} + \ominus = Cu^{\cdot}$, $Fe^{\cdot\cdot\cdot} + \ominus = Fe^{\cdot\cdot}$), oxidation at the anode (= removal of electrons: $Sn^{\cdot\cdot} - 2 \ominus = Sn^{\cdot\cdot\cdot\cdot}$). The polarisation E.M.F. then takes the value which would be shown by a correspondingly constructed oxidation-reduction cell.

(3) If the electrolyte liquid contains substances which can be oxidised by oxygen or reduced by hydrogen, then in an electrolysis in aqueous or aqueous-alcoholic solution it frequently happens that there is no evolution of oxygen or hydrogen, the gases being used directly in the nascent state for the oxidation or reduction process. (Cf. the anodic preparation of potassium perchlorate from potassium chlorate; of persulphuric acid from sulphuric acid; of chromate from chromium salts; or the cathodic preparation of isopropyl alcohol from acetone, or of hydrazo- and azo-benzene and aniline from nitrobenzene.) When the process is capable of taking place in several steps (cf. the reduction of nitrobenzene just referred to), then with definite concentrations a definite oxidation or reduction potential corresponds to each step, according to equation (84). This leads to the possibility, under some circumstances, of adjusting the potential to the proper value to carry the process just as far as the desired product.

(4) It is often possible by electrolysis to carry out oxidation or reduction processes which cannot be done with the highest oxygen or hydrogen pressures that can be used technically. The superiority of the electrochemical method can be due to two different causes:

(α) The *equilibrium* for the process in question may be unfavourable at the gas pressures which can be applied. The practicability of the process by an electrochemical method then depends upon the fact that as a result of the over-voltage phenomenon hydrogen and oxygen are available in a state thermodynamically corresponding to the gases under a pressure of millions or even billions of atmospheres.

The meaning of "over-voltage" is as follows: at a *platinised* platinum electrode it is actually possible to cause an evolution of hydrogen at 1 atmosphere from a $H^{\cdot}$ solution of definite concentration, with a cathode potential equal to the potential taken up by the same electrode charged with hydrogen at 1 atm. in an acid solution of the same concentration. But if other metals are used for the cathode, e.g. *bare* platinum, lead or mercury, the evolution of hydrogen requires a considerably higher potential. The excess of this over the reversible potential at the platinised electrode is called "over-voltage". It must

be assumed that in the intermediate stage before the evolution commences the gas is in a state of enhanced capacity for performing work. The E.M.F. of a gas-concentration cell (ionic concentrations equal, gas pressures different at the two electrodes) is in the case of hydrogen

$$E = \frac{RT}{2F} \log_e \frac{p_1}{p_2} \quad . \quad . \quad . \quad . \quad (85)$$

since the work of expansion for the isothermal and reversible transfer of 1 mol of gas from a higher to a lower pressure

$$= RT \log_e \frac{p_1}{p_2},$$

and for the same transfer in the cell 2F is caused to move:

$$(1H_2 - 2 \ominus = 2H^{\cdot}).$$

For oxygen

$$E = \frac{RT}{4F} \log_e \frac{p_1}{p_2} (1O_2 + 2H_2O + 4 \ominus = 4OH').$$

Thermodynamically therefore the increase in free energy corresponding to an over-voltage of 0·029 volt $\left(= \frac{0{\cdot}058}{2}\right)$ can with hydrogen be taken as equivalent to a ten-fold increase in the pressure, and with oxygen to a hundred-fold increase. The over-voltage of hydrogen at Hg amounts to 0·44 volt, and is therefore equivalent to a pressure of 10^{15} atm.

(β) The reason for the superiority of an electrochemical oxidation or reduction process may also lie in the fact that in spite of the position of the equilibrium being favourable, the *velocity* of the reaction with molecular oxygen or hydrogen is very small. In the electrolysis cell the velocity is sometimes much greater, either because of a catalytic influence of the electrode metal, or because of the special way in which at the moment of discharge of the ions, the atomic hydrogen or oxygen is immediately utilised in the process in question.

(5) In order to obtain a definite product, when different oxidation or reduction products are obtainable from the same original materials, it is usually necessary to regulate the electrode potential, as already mentioned. Instead of this exact method the rougher method of regulating the *current density* (= current strength per sq. cm. of electrode surface) is more usual, since with increasing current density the anode or cathode potential also rises, as a result of the increasing polarisation. The current density most suitable for obtaining a given reaction product is

found empirically. The electrolysis is then carried out with a current strength depending upon the size of the electrodes.

References :—

Eucken, Jette, and Lamer. §§ 248-53.
Nernst. Bk. IV, Chap. VIII, p. 868 *seq.*
Le Blanc. Chap. VIII (over-voltage, p. 298).
Allmand and Ellingham. Applied Electrochemistry, 2nd edition (1924).

A. REDUCTION OF NITROTOLUENE (-BENZENE) TO AZOTOLUENE (-BENZENE)

(a) Experimental

(1) The construction of the apparatus, its contents, and the circuit are shown in Fig. 71 : in the centre of a tall beaker (1 l.) stands a porous clay cell of 6 cm. diameter. Inside this there is an anode consisting of a roll of lead foil, and as anode liquid a hot saturated sodium carbonate solution. The cathode consists of a fine mesh nickel wire gauze 5 cm. wide, lying closely round the porous cell. The cathode solution consists of 200 c.c. 70 per cent alcohol (methylated spirit may also be used) in which 5 gms. of sodium acetate (to increase the conductivity) and 20 gms. nitrotoluene (18 gms. nitrobenzene) are dissolved. Both solutions are put in at 70°. The heat developed during the passage of the current is then sufficient to maintain the necessary temperature. Round the upper part of the beaker are several windings of rubber tubing carrying a stream of tap-water, so that most of the alcohol which is vaporised condenses on the upper part of the walls of the vessel. Any loss which takes place in spite of this is made good by addition of a 70 per cent. alcohol. The anode must be freed before use from any adhering layer of the brown dioxide, so that the bare metal surface shows. There must be good metallic contact everywhere ; this should be looked to especially at the binding screw connecting

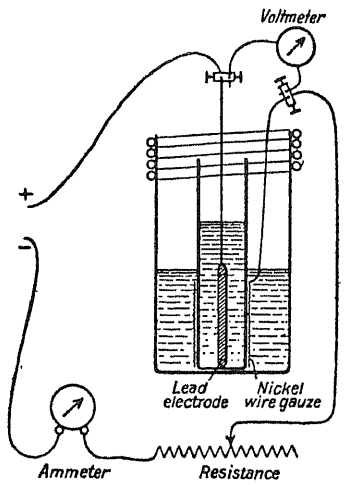

FIG. 71.

the leads to the lead anode. When connecting up the measuring instruments (ammeter in the current circuit; voltmeter in parallel with the cell) care must be taken that the signs are right.

(2) With the cathode dimensions given the reduction is done with 6-7 ampères and lasts from 130 to 160 minutes. It is complete as soon as hydrogen is evolved in the form of bubbles at the cathode. (Not to be confused with the alcohol vapour bubbles which, particularly at the beginning, rise from *all parts* of the liquid. The moment of the commencement of hydrogen evolution may be calculated beforehand from the quantity of electricity corresponding to the amount of substance taken and the current strength, and usually agrees remarkably well with observation.) The current strength is then reduced to about 2 amps. and the electrolysis continued until the hydrogen evolution is renewed; thereby, since the evolved hydrogen caused a vigorous stirring of the cathode liquid, parts of the liquid still remaining unreduced are eventually reduced. Usually hydrogen evolution begins again after only a few minutes. The anode becomes covered during electrolysis with a dark layer of PbO_2. The current strength is recorded, and the corresponding duration to the nearest half-minute, and from these data the quantity of electricity passed is calculated in coulombs or ampère-hours. With a variable current strength, it is recorded every five minutes and the mean taken.

The porous cell is removed and a vigorous air stream is blown through the cathode liquid for *ca.* quarter of an hour, to oxidise any hydrazo compound formed to the azo compound. After cooling the azotoluene is filtered off with suction, and crystallised from petroleum ether. By diluting the mother liquor with water the (less pure) remainder can be precipitated out. If the reduction product appears in an oily form, crystallisation may be induced by inoculating with a crystal of azotoluene, or by scratching the walls of the vessel with a glass rod. Also on standing in the ice-chest crystallisation usually begins spontaneously.

(b) Calculation of the yield and the current efficiency

According to the equation

$$2CH_3(C_6H_4)NO_2 + 8H^{\bullet} + 8\ominus = CH_3(C_6H_4)N = N(C_6H_4)CH_3 + 4H_2O \quad (86)$$

there should be produced in the cathode space, from 2×137 gms. nitrotoluene by the introduction of $8 \times 96494 = 7{\cdot}72 \times 10^5$

coulombs (214·4 amp. hrs.) 210 gms. azotoluene; therefore from 20 gms. 15·32 gms. azotoluene (from 18 gms. nitrobenzene 13·27 gms. azobenzene) by the employment of $5{\cdot}64 \times 10^4$ coulombs = 15·65 amp. hrs.

Hence, if in an experiment in which a current strength of 7 ampères was applied for 144 minutes, 13·5 gms. azotoluene (recrystallised product) were obtained from 20 gms. nitrotoluene the yield would be $\frac{13{\cdot}5}{15{\cdot}32} = 0{\cdot}88 = 88$ per cent.

For complete reduction of the amount of nitrotoluene used 15·65 amp. hrs. are necessary; 16·80 amp. hrs. were used. The current efficiency is therefore $\frac{15{\cdot}65}{16{\cdot}80} = 93{\cdot}2$ per cent.

After the experiment the porous cell is cleaned from the soda solution with hot water, for the sake of preserving it.

B. OXIDATION OF CHROMIUM SULPHATE TO CHROMIC ACID

(a) Theory

The process at the anode corresponds to the equation:

$$Cr_2(SO_4)_3 + 8H_2O - 6\ominus = 2H_2CrO_4 + 3H_2SO_4 + 6H^{\cdot} \quad (87)$$

Or if only the ions taking part are considered:

$$2Cr^{\cdot\cdot\cdot} + 8H_2O - 6\ominus = 2CrO''_4 + 16H^{\cdot}.$$

Simultaneously water is decomposed at the anode with evolution of oxygen. This effect is initially very slight, but increases in proportion as the solution is depleted of chromium salt and enriched in chromic acid. Correspondingly the current efficiency exceeds 90 per cent. of the theoretical during the early part of the experiment but diminishes greatly as soon as any considerable part of the chromium salt has been oxidised. For the experiment to proceed according to the above equation the current density must be progressively decreased. At the cathode hydrogen is evolved almost quantitatively

$$6H^{\cdot} + 6\ominus = 3H_2$$

since in the acid solution the $H^{\cdot}$ ions are discharged more easily than $Cr^{\cdot\cdot\cdot}$ ions, and the partial reduction of $Cr^{\cdot\cdot\cdot}$ ions to $Cr^{\cdot\cdot}$ ions (reduction of chromic to chromous salts) takes place only with difficulty. A small deficit of hydrogen is found, without detectable amounts of Cr^{II} salts being formed. This is explicable by the property of chromous salts of absorbing oxygen rapidly

from the air to form chromic salts. The yield of chromic acid is determined, and the course of the reaction followed by titrating samples with sodium thiosulphate.

(b) Experimental

A cylindrical lead vessel contains a porous cell, in which a cylindrical lead anode stands; the lead vessel itself serves as cathode. The anode and cathode liquid is a solution of a salt of chromium oxide prepared as follows: 200 gms. chrome alum $KCr(SO_4)_2 . 12H_2O$ are dissolved in hot water, treated with 150 c.c. concentrated sulphuric acid, and made up to 1000 c.c. This solution is poured in while still warm. The apparatus is placed in a jar with warm water and electrolysed with a current density of 2 to 3 amps. per 100 sq. cm. anode surface at a temperature of from 40° to 60°. The oxidation is done in the fume cupboard. The source of current is at 4 to 10 volts; a voltmeter is connected in parallel with the cell. Before the regular oxidation begins the anode becomes covered with a layer of lead dioxide (PbO_2 catalytically accelerates the formation of chromic acid).

Before taking each sample the anode liquid is *well stirred*. The sample is mixed with water, heated to boiling to drive out dissolved oxygen and ozone, made up to 100 c.c. with cold water, and cooled. Potassium iodide is added and the iodine formed titrated in the usual way with sodium thiosulphate. The change in volume of the anode solution through the removal of samples and through vaporisation can be taken into account in the calculation.

(c) Calculation of the current efficiency

The amount of CrO_3 to be expected (from Faraday's law) per unit current and in a definite time is calculated. From the titrations is found the increase in CrO_3 for each interval of time. The ratio of these numbers to the number expressing the greatest increase theoretically possible in the given time interval, multiplied by 100, gives the percentage current efficiency. Curves are drawn for the current efficiency against time and for the absolute quantity of CrO_3 against time.

XIX. THE LEAD ACCUMULATOR

(a) Theory

(1) THE chemical processes occurring when a lead accumulator is discharged or charged can be represented by the following equation:

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O \quad . \quad (88)$$

During discharge the reaction proceeds spontaneously from left to right, and when being charged the process from right to left is caused to take place by the application of an external E.M.F. The E.M.F. of the accumulator for these two changes can be calculated from the maximum work which the process is able to yield when taking place reversibly. Since the reaction in the sense of the equation above is connected with the transport of 2F, the electrical work amounts to 2 . E . F. This must be equal to the maximum work, given thermodynamically as

$$A = 2 \,.\, E \,.\, F = RT \log_e K'' - RT \log_e \frac{[PbSO_4]^2[H_2O]^2}{[Pb][PbO_2][H_2SO_4]^2}.$$

(The square brackets refer to concentrations in the solution.) Since the solid phases Pb, PbO_2 and $PbSO_4$ are not completely used up either by charging or discharging, the negligibly small concentrations of dissolved Pb, PbO_2, and that of the undissociated $PbSO_4$ remain constant, and are therefore without influence upon the value of the maximum work. Hence for the maximum work the simpler formula holds:

$$2 \,.\, E \,.\, F = RT \log_e K' - RT \log_e \frac{[H_2O]^2}{[H_2SO_4]^2}$$

or

$$E = \frac{RT}{F} \log_e K - \frac{RT}{F} \log_e \frac{[H_2O]}{[H_2SO_4]} \quad . \quad (89)$$

($K = \sqrt{K'}$.) The E.M.F. is therefore dependent *only* upon the ratio of the concentrations of water and of sulphuric acid, i.e. upon the *degree of dilution of the aqueous sulphuric acid*, and increases with the concentration of the sulphuric acid. This

can also be seen qualitatively from (88), where the tendency of the process to take place from left to right is greater, the higher the sulphuric acid concentration. Since according to (88) during discharge sulphuric acid is used up and water produced, the E.M.F. falls in the course of this process, and rises during charging because of the increase in the sulphuric acid concentration.

(2) The connexion between potential difference and sulphuric acid concentration can also be arrived at qualitatively by a consideration of the single potentials. The Pb plate sends $Pb^{\cdot\cdot}$ ions into the solution the more readily, and is therefore the more negative with respect to the PbO_2 plate, the smaller the $Pb^{\cdot\cdot}$ ion concentration. Since solid lead sulphate is always present, the product $[Pb^{\cdot\cdot}] \times [SO_4'']$ must always be constant, so that the $Pb^{\cdot\cdot}$ concentration is smaller, the higher the SO_4'' concentration. On the other hand, the greater the concentration of $Pb^{\cdot\cdot\cdot\cdot}$ in the solution the more positive is the PbO_2 plate with respect to the Pb plate. The presence of PbO_2 as a solid phase involves constancy of the solubility product $[Pb^{\cdot\cdot\cdot\cdot}] \times [OH']^4$. Increase of the $Pb^{\cdot\cdot\cdot\cdot}$ concentration is therefore connected with a decrease in the OH′ concentration, and since the ionic product of water is constant, must run parallel with an increase in the $H^{\cdot}$ concentration. It follows therefore that the Pb plate is more negative and the PbO_2 plate more positive, i.e. the total potential difference of the accumulator is greater, the more concentrated the sulphuric acid. (The setting-up of the potential at the PbO_2 plate can also be considered from the standpoint of the OH′ ions, by considering it as an electrode which sends OH′ ions into the solution. This way of looking at the matter also gives the single potential as more positive the smaller the OH′ concentration, and the larger therefore the $H^{\cdot}$ concentration.)

(3) The processes which occur during the discharging and charging may be formulated more exactly :

(*a*) Discharge (Galvanic cell) :

(α) Pb plate (— pole ; anode) :

$$Pb - 2\ominus = Pb^{\cdot\cdot};$$
$$Pb^{\cdot\cdot} + SO_4'' = PbSO_4;$$

(β) PbO_2 plate (+ pole ; cathode) :

$$PbO_2 + 2\ominus + 4H^{\cdot} + SO_4'' = PbSO_4 + 2H_2O;$$

(*b*) Charging (Electrolytic cell) :

(α) Pb plate (— pole ; cathode) :

$$PbSO_4 + 2\ominus = Pb + SO_4'';$$

(β) PbO_2 plate (+ pole ; anode) :

$$PbSO_4 - 2\ominus + 2H_2O = PbO_2 + 4H^{\cdot} + SO_4''.$$

(4) If the potential difference of the accumulator, with the same concentration of acid (as measured) is compared during charging and discharging, it is always higher whilst charging than whilst discharging. The reason for this is to be sought in the fact that *in the immediate neighbourhood of the porous surface of the plates*, where the chemical changes described take place, the acid concentration is always greater when charging and smaller when discharging, *than in the free space between the electrodes*. As a consequence of this concentration difference liquid potentials appear which are of importance in connexion with the difference of the E.M.F. when charging and discharging.

(5) The highest value of the E.M.F. of the lead accumulator is given by the decomposition potential of the sulphuric acid solution. When this is reached, electrolysis of the water begins, as is indicated by small gas bubbles rising up. The fact that electrolysis begins at 2·3 volts, while between platinised platinum electrodes it takes place at only 1·67 volts, is due to the over-voltage of hydrogen at lead, which has the high value of 0·6 volt (cf. p.215).

References : —

Eucken, Jette, and Lamer. § 252.
Nernst. Bk. IV, Chap. VII, p. 847 ; Chap. VIII, p. 871.
Le Blanc. Chap. IX.
Allmand and Ellingham. Applied Electrochemistry, 2nd edition (1924). Chap. XIV.

(b) Instructions for use

Every accumulator when purchased is accompanied by instructions for use issued by the factory. This includes information about the highest permissible charging and discharging current, the capacity in ampère-hours, and usually also the concentration of the sulphuric acid in the charged and the discharged state. By the *capacity* is here meant the quantity of electricity which can be taken from an accumulator before the E.M.F. has fallen to a certain minimum E.M.F. (usually 1·8 volts), from the highest value reached by charging up. This minimum should not be overstepped, or the plates will be damaged. The capacity varies with the strength of the discharge current, being greater when the current strength is low. The reason for this is that with higher current strengths the sulphuric acid in the interior of the porous plates and in their immediate neighbourhood is used up so quickly that during the discharge diffusion does not produce complete equalisation of concentration with the unused acid between the plates ; con-

sequently the E.M.F., which is governed by the concentration of acid immediately in contact with the plates, reaches the value 1·8 volts sooner than with a smaller discharge rate, when a more complete equalisation of concentration by diffusion can take place. These diffusion processes are also the cause of the "recovery" of an accumulator. For example, if the voltage has fallen to 1·9 volts under a high rate of discharge, it rises again within a short time after disconnecting to 1·95 or 2·0 volts, because during the period of rest an equalisation of concentration takes place between the diluted acid in the interior and immediately at the surface of the plates, and the more concentrated acid between the plates.

(c) Experimental

The *efficiency* of an accumulator is to be determined in terms of the quantity of electricity and of electrical energy. By the "efficiency" is meant the ratio between the number of coulombs or joules put in and the number taken out. The quantity of electricity is measured in coulombs = ampère-seconds, or in ampère-hours (1 amp. hr. = 3600 amp. secs.). The electrical energy is measured in joules = watt-seconds, or in watt-hours (1 watt-hr. = 3600 watt-secs., cf. p. 146). Hence the quantities to be measured during the charge and discharge are the current strength, the potential difference and the time. The current strength is measured with an ammeter, the potential difference with a voltmeter and the time with a watch.

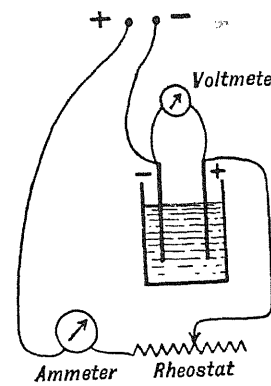

FIG. 72.

(1) CHARGING

A discharged accumulator of 1·8 volts E.M.F. is used, and connected in series with a rheostat to the measuring instruments, as in Fig. 72, and to the charging battery. Since the accumulator during charging acts as an electrolytic cell, the direction of the current everywhere in the circuit is governed by the poles of the charging battery. The ammeter is in the main current circuit, the voltmeter in parallel with the accumulator.

After connecting up the rheostat is adjusted so that the current strength is 1·5 amps. The exact time of switching on is recorded, and also the readings of voltage and current strength every five minutes. The current is regulated to be as constant as possible during the whole experiment at 1·5 amps. The subsequent calculation is greatly simplified thereby.

Although the voltmeter shows 1·8 volts[1] before switching on the charging current it rises immediately on switching on to 2·0 to 2·1 volts. The reason for this is that in addition to the potential difference of the discharged accumulator, there is also to be added the Ohm's law fall of potential occurring in virtue of the charging battery, across the internal resistance of the accumulator. If the latter is equal to W_i and the current strength is 1·5 amps., this fall in potential must be $= 1{\cdot}5 \times W_i$ volts. With the current strength given and the size of accumulator usual for this purpose it amounts to 0·2 to 0·3 volt, from which the internal resistance of the accumulator is calculated to be from 0·13 to 0·2 ohm. In the course of the charging the concentration of sulphuric acid, and hence also the conductivity, rises—i.e. the internal resistance decreases, so that the potential difference in question continuously becomes smaller. If the connexion to the charging battery is frequently interrupted for a short time, the amount by which the P.D. then read on the voltmeter falls becomes smaller and smaller as the charging proceeds.

The charging is continued until there is vigorous evolution of gas. (Potential difference *ca.* 2·5 volts.) The charging battery is then disconnected, the exact time recorded, and the circuit altered as described below for the discharge.

(If an accumulator is discharged too far (a thing to be avoided) by an oversight—say to 1·6 or 1·5 volts—it is possible for the sulphuric acid to be so far used up that the internal resistance becomes quite considerable—up to 0·5 ohm. When the charging is begun, with a charging rate of 1·5 amps., there is a potential drop over this resistance, on account of the charging battery of $1{\cdot}5 \times 0{\cdot}5 = 0{\cdot}75$ volts. The voltmeter then shows an abnormally high reading, up to 2·5 volts or more, because in the immediate neighbourhood of the plates the acid concentration alters quickly, while for some time afterwards the lower concentration and the high resistance remains between the plates. But the potential difference rapidly decreases again as with

[1] The difference between the potential difference across the terminals and the E.M.F. may be neglected in this case. Cf. p. 226.

further charging new sulphuric acid is formed and the conductivity increases.)

(2) DISCHARGING

The accumulator, ammeter, voltmeter and resistance are connected as in the circuit of Fig. 73. Since now it is the accumulator which functions as the source of current, it is the poles of the accumulator which govern the direction of the current in the whole circuit. The strength of the discharge current is also adjusted to 1·5 amps. The ammeter and voltmeter are read every five minutes, and recorded (even when there is no change). The beginning and the end of the discharge are timed with the watch, the experiment being ended when the potential difference measured with the discharging circuit closed begins to fall *below* 1·8 volts; further discharge is harmful to the accumulator.

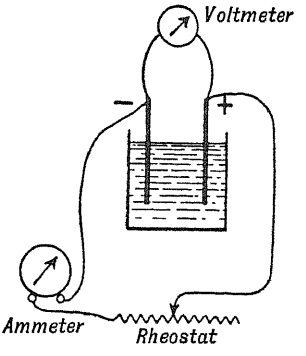

FIG. 73.

It must be noticed that what is being measured with the voltmeter is the so-called "discharge potential" which in general is to be distinguished from the E.M.F. The discharge potential is the part of the E.M.F. of the accumulator which falls over the resistance of the external circuit. The discharge potential is related to the E.M.F.—which falls over both the external resistance W_e and the internal resistance of the accumulator ($= W_i$)—in the same way as the external resistance is related to the total resistance of the current circuit:

$$\frac{\text{Discharge potential}}{\text{E.M.F.}} = \frac{W_e}{W_i + W_e} \quad . \quad . \quad (90)$$

or

$$\text{Discharge potential} = \text{E.M.F.}\ \frac{W_e}{W_i + W_e}.$$

If W_e is very large in comparison with W_i, then W_i can be neglected in the denominator in comparison with W_e, i.e. with a large external resistance the discharge potential is practically equal to the E.M.F. This is the case when the E.M.F. is measured with a voltmeter; the resistance is usually one or more thousand ohms, i.e. very large in comparison with the internal resistance of the accumulator (0·1 to 0·5 ohm.). The potential difference read is then practically equal to the E.M.F.

If on the other hand the external resistance is comparatively small, there is a distinct difference between the discharge potential and the E.M.F. Suppose that in addition to the voltmeter the discharge circuit is connected up; in order to obtain 1·5 amps., about 1·3 ohms must be included. The discharge potential is then equal to $\frac{1 \cdot 3}{0 \cdot 2 + 1 \cdot 3} \times \text{E.M.F.} = \text{E.M.F.} \times \frac{13}{15}$. If the voltmeter connected in alone (on open circuit) shows about 2·1 volts, it will only show $2 \cdot 1 \times \frac{13}{15} = 1 \cdot 8$ volts when the discharge circuit is closed.

Since only the discharge potential is available for the performance of external work, it is this quantity, not the E.M.F., which is to be measured when determining the rate of working of an accumulator, and when calculating the energy yield.

(d) Calculation of the efficiency

(1) Current Balance

If the current strength has been carefully maintained at the same value (1·5 amps.) during the charging and discharging, then the quantities of electricity put in and taken out are in the ratio of the corresponding times:

$$\text{Current yield} = \frac{\text{Time of discharge}}{\text{Time of charge.}}.$$

If the current strength was not constant, it is best to draw curves (abscissæ: time; ordinates: ampères, cf. Fig. 74). The total quantity of electricity is then proportional to the area contained between the co-ordinate axes, the curve, and the straight line which bounds the curve and passes through the time-point corresponding to the end of the experiment. This area can be determined either by the use of millimetre paper (by counting the sq. mm.) or by cutting out the surface, weighing it, and comparing with the weight of 1 sq. cm. of the same paper, or finally by calculation only, by dividing up the duration of the experiment into small time intervals, during which the current strength is taken as constant, or as altering so uniformly

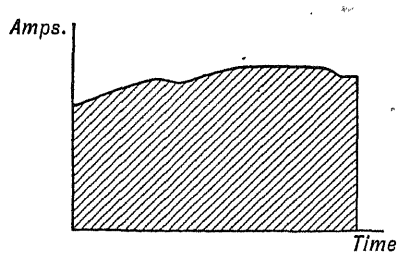

Fig. 74.

that a mean value can be assumed for it. The separate time intervals are multiplied by the corresponding current strengths, and all these separate products are added. If all the separate time intervals are of equal length, the mean of all the current strengths can be taken, and multiplied by the total duration.

(2) Energy Balance

This is calculated by means of time—potential difference curves for the charging and the discharging, which are drawn on the basis of the recorded notes of the experiment. Abscissæ: time; ordinates: potential difference. If the current strength has been constant and the same in both cases, the ratio of the two areas is equal to the ratio of the energy taken out to the energy put in. The determination of the areas is done by one of the methods given under (1). From the areas of the curves the actual electrical energy is obtained, in watt-seconds or joules, by multiplying the total area (volt × seconds) by 1·5 amps. An area of 1 volt × 1 second therefore corresponds in this case to 1·5 watt-seconds, and an area 1 volt × 1 hour to 1·5 watt-hours. If the current strengths were different for the charging and the discharging, but in each case *constant*, then 1 volt × 1 second might correspond, e.g. in the first experiment to 1·2 watt-seconds, and in the second to 1·5 watt-seconds. If the current strengths during the charging and the discharging were different and *variable*, then the third method of calculation given above must be used: the total time is divided up into small sections, within which both the current strength and the potential difference either remain constant or change uniformly. Multiplication of the time in seconds by the constant (or the mean value of the) corresponding current strength and potential difference, and addition of all these partial amounts gives the desired quantities.

Record the curves and numerical data for the quantities of electricity and of energy for the charging and the discharging; the current balance and the energy balance.

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